AL-FARABI KAZAKH NATIONAL UNIVERSITY

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INTRODUCTION TO THE PHYSICAL MATERIAL SCIENCE

Education manual

Almaty
«Kazakh university Press»
2015

UDC 620
BBC 30.3
P 92

Recommended to print the scientific session of the physico-technical faculty of Al-Farabi Kazakh national university and editorial -printing session

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Prikhodko O.Yu., Ismailova G.A.
P 92 Introduction to the physical material science: Education manual / O.Yu. Prikhodko, G.A. Ismailova. – Almaty: Қазақ университеті, 2015. – 187 с.
ISBN 978-601-04-1650-5

«Introduction to the physical material science» This manual is dedicated for the study of regularities and mechanisms of materials phase formation in equilibrium and non-equilibrium conditions, dependence of their properties from the ways of creating materials with desired properties. In the manual also describes the main physical properties of metals, semiconductors and dielectrics, features of chemical bondings in the material.

ISBN 978-601-04-1650-5

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FOREWORD

The progress of human civilization connected with the progress in development, obtaining and using of different materials. New materials enhanced the work efficiency. Today special significance acquired materials and devices, which designed to increase the effectiveness of mental labor, to ensure progress in computer technology, methods of storage and transmission of information, automation of industry, efficiency conversion of various types of energy with high efficiency PEC.

Physical material science – is a scientific discipline that studies the laws and the atomic mechanism of material's phase formation (metals, semiconductors, dielectrics, etc.) in equilibrium and non-equilibrium conditions, the dependence of bulk and surface properties of these materials on the nature of chemical bonding, chemical and phase composition, structural imperfections and ways of creating materials with desired properties and management of the latter by the action to the chemical composition, phase and structural state of the material.

The aim of course is the study of regularities and mechanism of material's phase formation (metals, semiconductors, dielectrics, etc.) in equilibrium and non- equilibrium conditions, depending on their properties to the nature of chemical bonding, chemical and phase composition and ways of creating materials with desired properties.

Important information about the phase composition of alloys in equilibrium and similar conditions, about beginning temperatures and end of phase transformations can be obtained from state diagrams.

The state diagrams of binary and ternary systems in combination with the composition-property diagrams are the basis of the doping theory and the creation of alloys with desired properties.

For materials scientists and specialists in related fields state diagrams – is a base for new searching and improvement of existing materials. For metallurgists state diagrams are the basis for the development and improvement of metallurgical processes of obtaining metals and compounds, also their purification from impurities.

INTRODUCTION. TASKS OF THE COURSE «INTRODUCTION TO THE PHYSICAL MATERIAL SCIENCE»

Development of materials with desired properties requires a clear understanding of what factors depend these properties and how, and how at least they can be controlled.

The properties of materials depended on many factors and determined, at first, by the nature of chemical bonding; phase state of materials; type, concentration and nature of the impurities. Very strong influence on the properties of the materials have defects in the atomic structure, their interaction with each other and with impurities.

Historically, existed two approaches about interpretation of the properties and phenomena occurred in solids, particularly in metals:

– macroscopic or phenomenological;
– microscopic or atomistic.

For the macroscopic approach is typical solid interpretation as a continuum without detailing its internal structure. The approach connected with the resistance of materials and other sciences.

In the microscopic approach description and explanation of the properties of solids based on the laws of its constituent particle's interaction, i.e. at the atomic level. In this approach, realized following chain: structure – property. Today microscopic approach is the only strictly scientific approach to the interpretation of the observed properties and phenomena in solids.

In general case, for obtaining materials with desired properties it was necessary provide implementation of the following logical sequence:

Technology → atomic structure → (energy spectrum) → physicochemical properties → technology

The object of study in material science are high degree purified single crystals of semiconductors, which not found in nature, i.e. processed materials.

The theoretical foundations of physical material science include:

– periodic law of Mendeleev
– laws of thermodynamics,

– theory of chemical bonding,

– band theory of solids,

– position about the role of short-range order in the arrangement of atoms in formation of the semiconductors and dielectrics properties (was formulated at first by A.F. Ioffe).

Material science originated in the middle of 19th century. Leading scientists, who was initiating material science – is Anosov (1797-1831 yy.) and Chernov (1839-1921 yy.).

Formation of semiconductor material science started in the 30-40 years of 20th century under the direction of academician A.F. Ioffe.

In the 20 years in the USA developed ferroelectric properties of Rochelle salt.

In 1944, in the USSR academician Wool developed ferroelectric properties of barium titanate (BaTi).

In 1948–1949 yy. in the USA Bardeen, Shockley and Brayteyn – created the first transistor.

In the early 40-ies the USA launched the first atomic reactor.

In 1950– Till and Little obtained the first single crystal of germanium with instrument impurity.

In 1958 in the USA and USSR was marked by obtaining dislocation-free silicon.

In 1955–1960 yy. – development of space technology, which required the creation of new materials.

1960 years- USSR – the creation of the first solid-state laser generator on gallium arsenide (GaAs) (Basov, Nasledov, Rivkin).

1950 years USSR – development of chalcogenide vitreous semiconductors – CVS (Kolomiets, Goryunova).

1975 year- USA- were first obtained films of amorphous silicon (a-Si), and later the films of amorphous hydrogenated silicon (a-Si: H), (Speer, Le Comber).

1960-1970 yy. – the creation of theory and technology of heterostructures. (Zh.I. Alferov)

1970 yy. – the creation of VLIS – very large integrated microcircuits.

1980 yy. – the creation of extralattices (superlattices).

1990 yy. -opening of quantum size effects in solid, which was the beginning of the creation of lasers based on quantum wells and quantum dots.

Nowadays provide intensive research of new materials and developing new technologies and devices: composites, polymers, amorphous metals; powder metallurgy, radiation technology, high-temperature superconductivity; construction materials; fullerenes, nanotubes, nanowires; developed tools to nanomaterials. In Figure 1.1. showed the position of materials science in the general structure of science.

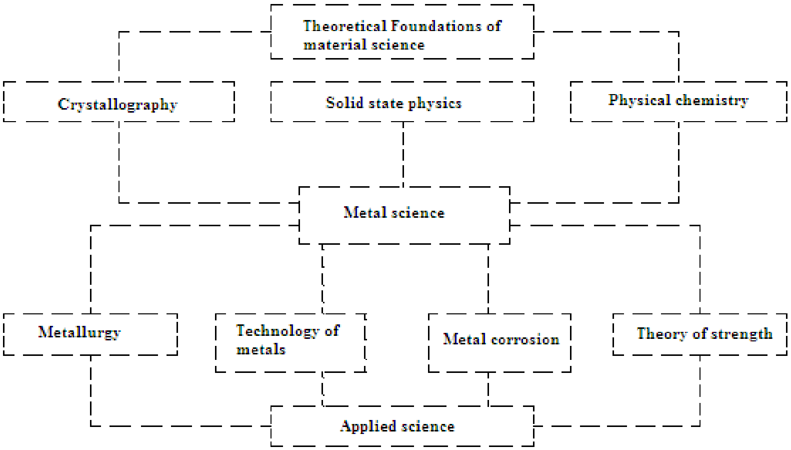


Figure 1.1.– The position of materials science in the general structure of science

The main tasks of the course "Introduction to the physical material science" is establishment of the relationship between the composition, structure and properties of materials, the study of thermal, chemical and thermal treatment and other methods of hardening, the formation of knowledge about the properties of the main types of materials and their application field.

Chapter 1

GENERAL PHYSICAL PROPERTIES OF SEMICONDUCTORS, DIELECTRICS AND METALS

§ 1. General provisions

The basic physical properties of semiconductors, dielectrics and metals, advisable to consider in order to facilitate understanding of the influence regularities to the properties of the material composition and obtaining technology.

Material properties of practical interest is very diverse, so we consider the properties of the most important materials used in semiconductor electronics. This group of properties we can classified as following:

Table 1.1. The basic physical properties of semiconductors, dielectrics and metals

Class properties	Basic phenomena and processes of this class properties
1. Electrical properties	The movement of charge carriers and their interaction with each other and with the environment
2. Electro-optical properties	Generation and registration (detection) of optical radiation, their interaction with the environment and various fields, mutual transformation of the electrical and optical signals
3. Electro-acoustic properties	Generation and registration (detection) of the acoustic oscillations, the transformation of electromagnetic energy into the energy of elastic waves
4. Magnetic properties	The emergence of different types of magnetism. The interaction of the magnetic moments of electrons with each other, with the moving electric charges and with the environment
5. Thermal properties	Vibrations of atoms (the motion of photons), their interaction with each other and the environment
6. Mechanical properties	Elastic and plastic deformations

In general, the properties of materials depend on three characteristics:

1. the nature of the chemical bonding;
2. the chemical composition and the phase state;
3. the degree of perfection of the atomic structure.

On the effectiveness of the influence of structural defects on the properties the properties can be divided into following groups:

a) structure-insensitive properties – virtually independent or very little dependent on structural defects, determined by the nature and strength of the chemical bonding;

b) the structure-sensitive properties – strongly changed under the influence of structural defects, their type and concentration. These properties are associated with the movement of particles or quasi-particles – atoms, electrons, phonons, grain boundaries, the boundaries of magnetic or electric domains and etc.

§ 2. Electrical properties

All materials in different degrees, conducted electric current, i.e. had electrical conductivity. On this basis the materials are divided into conductors, semiconductors, dielectrics.

In physics, the division into metals and non-metals is determined by the behavior of the electrical resistivity of the material: in metals is determined by the electronic structure of shells and at $T \to 0$ K, $\rho \to 0$, at the same time, in non-metals, i.e. in semiconductors and dielectrics at $T \to 0$ K, $\rho \to \infty$.

All substances due to electrical physical properties (specific resistivity ρ) can be divided into three major classes:

metals: $\rho = (10^{-6} - 10^{-4})$ Ом*см,
semiconductors: $\rho = (10^{-4} - 10^{10})$ Ом*см,
dielectrics: $\rho > 10^{10}$ Ом*см.

These intervals are relative, because under the influence of various factors limit values **ρ** may overlap. The conductivity of semiconductors **σ** is intermediate between metals and insulators.

The ability and the opportunity of the material to conduct electrical current is mainly depend on: the type of chemical bonding, the band gap, type of free charge carriers, their concentration and mobility.

The main parameters that characterize the electrical properties are: electrical conductivity **γ** (ohm^{-1} * m^{-1}); resistivity **ρ** (Ohm * m); the temperature coefficient of resistivity **α_ρ** (K^{-1}).

Conductivity γ connected the current density j (A/m^2) and the electric field strength E (V/m), causing the current ratio

$$j = \gamma E \tag{1.1}$$

(differential form of Ohm's law).

Electrical resistivity – the inversed magnitude of conductivity:

$$\rho = \frac{1}{\gamma} \tag{1.2}$$

where **γ** – conductivity, [**γ**] = [Sm/m], (См –Siemens).

The density of the current **j** is related with the charge **e** of current carriers, their number **n** and field strength by the relationship:

$$j = en\mu E \tag{1.3}$$

where μ – charge carrier mobility, numerically equal to the drift velocity of charged particles in the direction of the field strength in the 1V/cm, [E] = [1 V/cm]), [μ] – [cm^2 / (V*s)]. The mobility of the charge carriers depends on the type of chemical bonding, the temperature and structural imperfections and varies for different substances within the range of from 10 to 10^5 [cm^2 / (V*s)].

Structural sensitivity of the electrical conductivity caused by the influence of structural imperfections on the mobility of the charge carriers. In the presence of charge carriers in the material of different types (electrons, holes, or ions) the electric conductivity is determined by the expression:

$$\gamma = \Sigma\, en_i\mu_i \tag{1.4}$$

from which follows that the contribution to the electrical charge carriers electrical conductivity of this type depends on the concentration and mobility.

The mobility of the charge carriers is equal to:

$$\mu = \left(\frac{e}{m^*}\right)\left(\frac{l}{v}\right) = \frac{\tau e}{m^*} \tag{1.5}$$

where m^* – effective mass of carrier; l – length of free path; v – the thermal velocity of the movement of charge carriers; τ – mean free time or relaxation.

Then

$$\gamma = en\frac{el}{m^* v} = \frac{ne^2 l}{m^* v} \tag{1.6}$$

that is, the electrical conductivity is proportional to the concentration of charge carriers, their mobility, and the free-path length and inversely proportional to the effective mass. The free-path length of the electron is in the range $10^{-6} < l_{\text{см}} < 10^{-5}$ and the lower, the more violations of the periodic potential field of the ion core of crystal caused by the thermal vibrations of the atoms (dynamic distortion) or disordered atomic displacements caused by the dissolution of foreign atoms with atomic radius different from the matrix (static distortions).

The thermal electron velocity **v** at nondegenerate semiconductors at room temperature equals about 10 cm/s, and in metals, where the electron gas is degenerate, the rate approximately greater to order. Hence, the average wavelength of free electrons, depending on the de Broglie relation:

$$\lambda = \frac{h}{mv} \tag{1.7}$$

in semiconductors is approximately $7{*}10^{-7}$ cm, and in metal to one order less $5{*}10^{-8}$ cm, i.e. is the same order of magnitude as the interatomic distances. It follows that the electron scattering on point defects must be strongly expressed in metals, and extended defects (dislocations, sub-boundaries and grain boundaries) – in semiconductors.

In accordance with the physical nature of the charge carriers existed two main types of electrical conductivity: electronic and ionic.

Electronic electrical conductivity can be purely electronic (for metals), purely hole and mixed, when in the electrical conductivity involving both electrons and holes (semiconductors). Ionic conductivity may be cationic, anionic, and mixed.

Electronic conductivity have metals, semiconductors and dielectrics.

The electronic conductivity of dielectrics is observed only at very high voltages (near breakdown).

Ionic conductivity have liquid electrolytes and ionic crystals (alkali-halide, and others). An essential feature of the ionic conductivity is that it is accompanied by the transfer of substance.

The electrical conductivity depends on temperature, pressure, irradiation, impurities. The sharp dependence of the electrical conductivity of semiconductors from different types of affecting give them opportunity in the application as sensors.

Changes of electrical conductivity of metals under all kinds of impacts, including temperature changing associated with the change in charge carrier mobility. The higher the temperature, the greater the amplitude of the thermal vibrations of atoms (ions), the more the local distortions of electric field of the ion core lattice, the stronger the scattering of charge carriers and the greater the resistivity of metal.

In semiconductors increase in temperature and other effects affecting to the mobility of charge carriers as in metals, but at the same time it increases the carrier concentration, can change the bandgap and other characteristics. These changes affect to the resistivity of semiconductors more than changing the mobility of charge carriers. Therefore, in semiconductors resistivity versus temperature dependence is more complicated.

Affecting the deformation to ρ (resistivity) depends on the nature of the material, the type of deformation – elastic or plastic. During plastic deformation to ρ influence the type, concentration and distribution character of structural imperfections. Changing **ρ** of semiconductors under the influence of elastic deformation causes tensoresistive effect, which was used in the mechanical strain sensors. Plastic deformation and radiation increase the concentration of charge carriers and at the same time reduce their mobility, mostly first effect dominates, and **ρ** is reduced.

For body with a constant cross section S, resistance R and length *l*, ρ is determined by:

$$\rho = \frac{RS}{l} \tag{1.8}$$

According to the theory of electrical conductivity, γ can be expressed by the following formula:

$$\gamma = \frac{q^2 n\lambda}{m\upsilon} \tag{1.9}$$

Where q and m – respectively the charge and mass of the charge carrier (electrons in conductors, electrons and holes in semiconductors, ions in dielectrics); υ and λ – the speed and the length of free path of the charge carrier; n – charge concentration, i.e. the number per unit volume.

Changing the conductivity and consequently the resistivity in real materials related to the concentration change and length of free path of the charge carriers.

Under the influence of electric field the charge carriers acquire acceleration, and their speed is proportional to the field strength:

$$\upsilon = uE \tag{1.10}$$

Where u (m^2/ V*s) – charge carrier mobility- the ratio of the velocity of their directed motion caused by the electric field to the field strength. It is determined by

$$u = \frac{q\lambda}{m\upsilon} \tag{1.11}$$

from whence

$$\gamma = qnu \tag{1.12}$$

The value of the electrical conductivity strongly depends on the carrier scattering by imperfections of the crystal lattice – structural defects and phonons. In the result of scattering reduced length of free path, speed and mobility of charge carriers. The electrons in an isolated atom have a strictly defined discrete values of energy. In solid in the result of atoms convergence and the strong interaction electrons and nuclei splits the energy levels of atoms and their integration into energy zones (Figure 1.2).

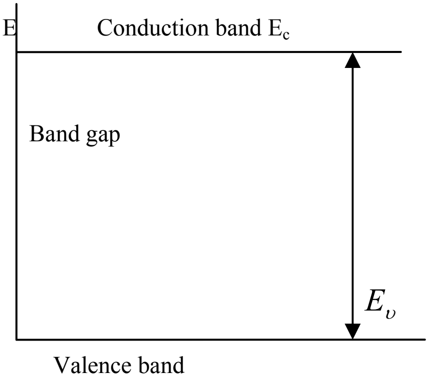


Figure 1.2. – Energy bands in solids

The energy band, where can present the charge carriers, called **permitted band.** Bands of energy, which may not be present carriers- **band gap.** During the formation of the solid from **n** atoms the discrete levels of the atoms are split into bands of allowed energies, which are separated by forbidden energy bands.

The maximum number of electrons on discrete levels of atoms equals:

levels	s	p	d	f
number of electrons	2	6	10	14

In metals at the top of the energy band is always present unfilled permitted energy states.

The Fermi level separates the filled part of the band from unfilled.

Energy band, resulting from the splitting of the levels of valence electrons is called *the valence band* (E_υ). After band of allowed energies – *the conduction band (E_c)*. Between them is *the band gap (E_g)*. When electron gets the energy exceeding the band gap, it passes from the valence band to the conduction band and participates in the electrical conductivity.

According to band theory of solids metals difference from non-metals is in the nature of the filling of the upper (last) energy bands. The most important feature of metals is that in them high energy band containing electrons (conduction band) is unoccupied levels. In dielectrics and semiconductors at low temperatures (close to 0 K) upper, entirely filled with electrons energy band (the valence band) is separated from the next – empty – band of allowed energies (the conduction band) with prohibited area $E_{\rm g}$ – bandgap, in which lacks the energy levels of electrons. In terms of the band theory of difference between semiconductors and dielectrics purely conventional: the value of $E_{\rm g}$, which separates the valence band and the conduction band in semiconductors and dielectrics is:

$$\begin{aligned} &E_g(\text{sc}) = \leq 2 \text{ эВ}, \\ &E_g(\text{diel.}) = \geq 2 \text{ эВ} \end{aligned} \qquad (1.13)$$

Existed also gapless semiconductors whose $E_{\rm g} = 0$, for example, HgTe and HgSe.

Impurities and defects in semiconductors and dielectrics may give rise to levels in the bandgap.

In semiconductors, the band created by the valence electrons are called valence (it is full at T = 0 K). The top of the valence band E_v. Blank band at T = 0 K after bandgap called the conduction band. The bottom of the conduction band is E_c (lowest energy).

According to the band model of semiconductors and dielectrics are not different. In practice, many semiconductors at low temperatures (near 0 K) behave as dielectrics, many dielectrics at high temperature is semiconductors.

According to the band theory solids are divided into conductors, semiconductors and dielectrics.

Conductors – materials in which the valence and conduction bands overlap or are adjacent to each other. Therefore, the electrons in the metal are free, i.e. can move from the valence band to the conduction band by applying a small electric field strength. The atoms in metals are connected with each other by *metallic bonding.* The valence electrons have high mobility because of the overlap E_υ and E_c can be easily moved in the lattice of metal crystal.

In metals observed *electronic type* of conductivity. This electrons was accelerated by the field transfer only charge. Mass transfer, such as in materials, which have ionic conductivity type does not occur.

ρ Range of metallic conductors takes three orders of magnitude from $1{,}58 \cdot 10^{-18}$ Ohm *m for silver until $1000 \cdot 10^{-8}$ Ohm * m for alloys system Fe – Cr – Al.

Semiconductors due to electrical properties have an intermediate place between conductors and dielectrics: their electrical resistivity is 10^{-6}-10^{9} ohm * m, the bandgap – from 0.05 to 2.5-3 eV. Atoms in semiconductors can be connected as a non-polar and polar covalent and ionic bonding, the type of electrical conductivity – *electron-hole.*

As dielectrics, semiconductors have negative temperature coefficient of resistance (TCR) α_ρ, i.e. with rising temperature ρ of semiconductors decreases, whereas ρ of metals increases.

An important feature of semiconductors is the high sensitivity of resistivity not only to heat, but also to other external influences (electromagnetic fields, radiation, etc.). This is due to the type of chemical bonding between atoms in the crystal lattice of the semiconductor, as well as presence of impurities and other defects even negligible concentrations which significantly affect to the concentration of free charge carriers and hence to the electrical properties of material.

At industry used semiconductors, which have *electron and hole* type of electrical conductivity.

In **dielectrics** bandgap higher than 3 eV, the electrical resistivity is $10^9 - 10^{16}$ Ohm * m. As in semiconductors, in dielectrics can occur covalent bonding type. A feature of the electrical conductivity of solid dielectrics is in most cases it is ionic character. Since $E_g >> kT$, only a very small amount of electrons can break away from their atoms by the action of thermal energy, and their contribution to the conductivity is negligible. *Ionic electrical conductivity* may be due to movement as an impurity ions and ions of the dielectric.

It should be noted that the electronic type of conductivity can be felt in the case if in the bandgap near the bottom of conduction band and top of valence band, respectively, will form a large number of donor and acceptor levels. The appearance of such levels may be due to the presence of impurities and crystal lattice defects.

Electronic conductivity, due to the presence of free electrons is manifested in strong electric fields and lead to insulation breakdown.

One of the major applications of metals and alloys in technique is using them as *conductors*. They are divided into two groups:

- Metals and alloys with high conductivity
- Metals and alloys with high resistance.

Metals and alloys with high conductivity is used for making the conductors, wires, cables, contacts, transformer windings, in integrated circuits for creating current carrying elements and others. The high electrical conductivity have pure metals – Ag, Au, Cu, Al and their alloys, some steels, bimetals. The main requirements to them – low resistivity and low temperature coefficient of electrical resistivity.

Metals and alloys with high resistance are used for the manufacturing of resistors, rheostats, electric heating devices, and others. These include copper alloys (constantan, manganin, nickeline) and alloys system of Fe – Ni – Cr, Fe – Cr – Al. Basic requirements for them: high ρ, low α_ρ and low thermoelectric power in tandem with copper. Furthermore, the alloys for electric heating devices have to be fire resistant.

Apart from these requirements as conductor and resistive materials must have a high mechanical strength, corrosion resistance and workability, i.e. processability pressure, welding, soldering, and other types of processing.

Changing values γ and ρ in real conductors is primarily due to the change in the length of free path λ.

The electrical conductivity of metals depends on the incompleteness of the valence shells, overlap of electron shells.

IB- subgroup (Ag, Cu, Au) and IIIB-subgroup (Al) elements of the periodic system have the highest electrical conductivity. This is due to the fact that the electrons easily move in the electron gas from incomplete s- shells. IA-subgroup elements, although they have the same structure of the outer s-shell exhibit lower conductivity due to the low conduction electron concentration (n), which is determined by the ratio of the crystal lattice parameters and diameter of the ion.

The transition metals have higher $\boldsymbol{\rho}$ than non-transition. In transition metals occurs overlap s- shells by unfilled d- and f- shells, which are energetically located below s – shells. When an electric field is applied occur scattering of s – electrons in the d – and f – bands, reducing their concentration in the conduction band.

Thus, the resistivity of pure metals are determined primarily by their nature, i.e. the concentration of conduction electrons. It does not depend on the temperature and the actual observed changes in ρ by varying the temperature associated with the change of the length of free path and the electron mobility.

During passage of the electron wave through an ideal (defect-free) lattice scattering do not occur. Crystal lattice defects is a cause of electrons scattering, resulting in the reduction of λ and, consequently, increase ρ.

Imperfections, which scattering electrons, can be divided into two groups:

– energetic defects (thermal vibrations of atoms or ions of lattice), determined by the temperature component (ρ_T) of material resistivity;

– defects of crystal structure, determined structural or residual (ρ_{res}) component of the resistivity of the material.

In this regard, the electrical resistivity of pure metal can be represented as

$$\rho = \rho_T + \rho_{res} \tag{1.14}$$

The impurity and intrinsic defects that violate the periodicity of the crystal lattice are the centers of scattering of electron waves. This reduces the length of free path λ and increases resistivity.

In a wide temperature range dependence of ρ from temperature is expressed as following:

$$\rho_T = \rho_0(1+\alpha t+\beta t^2+\gamma t^3+\ldots) \qquad (1.15)$$

In the temperature range for $t > \Theta_d$ (Θ_d-Debye temperature) ρ linearly depends on t:

$$\rho_T= \rho_0(1+\alpha t) \qquad (1.16)$$

Or during choice of absolute temperature scale

$$\rho_T= \rho_0 \alpha T \qquad (1.17)$$

where ρ_0 – resistivity at temperature taken as the reference point; T – the temperature (K); $\alpha = \alpha_\rho$ – temperature coefficient of resistivity.

Debye temperature separates the "low" temperatures area, in which quantum effects occur and where it is necessary to use quantum statistics, from the area of "high" temperatures.

In the differential form $\alpha_p = (1/\rho_0)\,(d\rho/dT)$.

At $T=T_m$ resistivity increases abruptly due to sharp decrease in the concentration of conduction electrons.

Some metals and alloys at temperatures close to 0 K, transfer to superconductive state i.e. their ρ sharply decreases almost to zero. In superconducting transition temperature (T_c)

$$\rho < 10^{-18}\ \text{Om*m}.$$

The theory of superconductivity based on the assumption that the electrons carrying the process of electrical conductivity connected Cooper pairs, the electrons in such pair have opposite directions of spins and impulses. Such binding of electrons is possible in the medium containing the positively charged ions, which weakens the field strength of the Coulomb repulsion between the electrons. The nature of the attraction forces between electrons is determined by their interaction with phonons. Movement of electron pairs can be viewed as the motion of one electron wave, which does not scatter by lattice points, and "wraps around" them. At T=0 all conduction electrons are connected. Rising of temperature and increasing of thermal vibrations leads to the rupture of the pair, and in T_c all pairs are destroyed, superconductivity disappears and the metal goes into a normal state with finite value of the electrical conductivity.

Unlike pure metals in the lattice of the alloy of main material arranged atoms of another element or formed other phases. In both cases they represent the scattering centers of electron waves.

For alloys, as well as for pure metals, performed dependence:

$\rho = \rho_T + \rho_{res.}$

For different types of alloys the dependence of the resistivity from the concentration of components forming the alloy is different.

Effect of solute on the electrical properties of alloy due to violation of the periodicity of the electric potential of main component lattice. These defects lead to scattering of electrons, decrease of the length of free path and, consequently, to increasing of ρ.

The degree of change of ρ depends on the nature of the main and impurity component – their valence and atomic diameter. The greater the difference between the valences and atomic diameters, the greater the increasing in ρ.

In the case of *unbounded solid solutions* of components A and B, if A and B – non-transition elements, $\rho_{ост}$ increases by dissolving B in A as A in B. In this change in ρ depending on the concentration of the components is characterized by symmetrical curve with maximum.

The dependence of the length of free path from the concentration of components A and B in the alloy is expressed by the relation:

$$\lambda = \beta/(c_A c_B) = \beta/(c_A(1 - c_A)) \qquad (1.18)$$

where β – coefficient of proportionality, constant for this system; c_A and c_B – respectively, the concentration of main and impurity component (at.%).

Substituting this expression into the formula $\rho = m\upsilon_T/(e^2 n\lambda)$, we obtain

$$\rho = m\upsilon_T c_A(1 - c_A)/\ (e^2 n\beta) \qquad (1.19)$$

By grouping the constant factors and denoting $m\upsilon_T/(e^2 n\beta)=D$, we obtain

$$\rho = Dc_A(1 - c_A) \qquad (1.20)$$

The function $c_A(1 - c_A)$ – parabola with maximum at $c_A= ½$, i.e. during equiatomic ratio of component in the alloy. Examples of such alloys are Ag – Au, Cu – Au, W- Mo.

The temperature coefficient of electrical resistivity of alloys is defined as same as for pure metals with using formula

$$\alpha_{p\ all} = (1/\ \rho_{0all})\ (d\ \rho_{all}\ /dT\ ) \qquad (1.21)$$

In isometric conditions $\alpha_{p\ all} \approx 1/\ \rho_{0all}$.

If one of the components of solid solution transition metal, the concentration dependence differs from parabolic. Because of s – d or s – f – electron scattering in transition metal maximum of ρ shifts toward higher concentrations of transition metal. If the transition metal are both components, then there is not only maximum displacement, but also took place velocity fluctuation of the curve.

The concentration dependence of the resistivity of *eutectic alloys* have linear character, as eutectic composed of phases, each of which has its own electronic structure, crystal lattice and concentration of conductive electrons. Eutectic phases can be pure metals, solid solutions or chemical compounds. In the case of changing concentration of components proportion of the eutectic phase change additive, as additive from one phase to another boundary phase and electrical resistivity of the eutectic. The electrical resistivity of eutectic two-phase described by ratio $\rho_{evt} = \rho_1\ c_1 + \rho_2\ c_2$, where ρ_1, ρ_2, c_1, c_2 – respectively, the electrical resistivity and concentration of the first and second phases.

In practice, there is disruption of the linearity of concentration dependence of ρ eutectics due to the presence of impurities, grain boundaries and other defects. The temperature coefficient of eutectic resistivity as α_p, of solid solutions, varies inversely with the concentration changes of ρ.

In contrast to solid solutions and eutectic *chemical compound* it is a brand new substance is fundamentally different in structure and properties of its constituent components (another type of crystal lattice, electronic structure, the concentration of charge carriers, sometimes another type of chemical bonding and electrical conductivity).

Metal films produced by vacuum methods (e.g., thermal evaporation, ion-plasma sputtering) used in microelectronics as interconnections, contact area, resistive and the magnetic elements, capacitor coatings.

The electrical properties of thin films are substantially different from those of the starting materials in bulk state. This is due to:

– structure of the films. At condensation of sprayed metal on the surface of the film structure can be changed from amorphous to crystalline;

– size effects. In the film prevail surface processes over bulky processes, especially if the film thickness (h) is comparable with the length of free path (λ) of majority charge carriers, which influence on the properties including electrical properties.

The resistivity ρ of the films is always above ρ_m due to the high concentration of defects.

The increase in ρ also contributes and size effect, i.e, decreasing the length of free path of electrons due to the scattering from the film surface.

The electrical properties of semiconductors

The most important elementary semiconductors, such as silicon and germanium, have the structure of the diamond, and many semiconductor crystals such as A^2B^6 or A^3B^5 (e.g., CdS, SdTe, GaAs, GaP, InSb, InP, AlP, AlSb, ZnS, etc.) have the structure of sphalerite type.

The main type of chemical bonding in semiconductors – is covalent bonding. Typically, covalent bonding (covalent non-polar) occurs when the socialization of valence electrons of neighboring atoms and elements observed in IVB-subgroup of the periodic system (Si, Ge), where each atom has four valence electrons. To form the connection each atom can take four electrons from each of four neighboring atoms and can also give them the same number of electrons, while remaining electrically neutral. Thus, occur exchange of electrons between atoms with forming stable eight electron valence shell of each of them.

Also the class of diamond-like compounds include A^3B^5 compound semiconductors, which form by IIIB- (B, Al, Ga, In) and VB- (N, P, As, Sb) subgroups elements of the periodic system and counterpart electronic analogues of Si and Ge. The atoms of III group elements have three valence electrons, while V group elements have five. Thus, to one atom in these compounds have an average of four valence electrons. Since the electron cloud in this regard, strapped to more electronegative atom B, it is not completely covalent and partially ionic (such bonding called covalent polar). Where A is charged positively and B negatively.

Even more ionic component of chemical bonding expressed in A^2B^6 compounds (ZnTe, ZnSe, CdTe, CdS, etc.). Finally, there are semiconductors with ionic bonding – are lead chalcogenides (PbS, PbSe, PbTe).

Qualitative characteristic of chemical bonding compound is its average atomic number Z_{av}.

For simple compounds A^3B^5 and A^2B^6

$$Z_{av} = (Z_A + Z_B)/2 \tag{1.22}$$

Within a class of compounds with increasing Z_{av} increases tendency of transistion from covalent to ionic bonding. This leads to the reduction in bonding strength; decreases also bandgap, melting point, resistivity.

The charge carriers. Intrinsic carrier. As a result of the electron exchange between atoms in the formation of covalent bonding the electrical conductivity does not occur, as the electron density distribution is fixed (two electrons for bonding between each pair of neighboring atoms). Under the influence of external effects (e.g., heating, irradiation) can occur rupture of one of the bondings, and electron leaves it, becoming free in crystal. He moves randomly through the crystal in the absence of an electric field. The absence of electron from one of the atom bondings is called the hole, and means that there is positive charge, which equal in value to the charge of past electron. The hole, as well as the electron moves randomly through the crystal, since the electron of neighboring bonding may take the place of the departed electron.

Semiconductor, which electrical conductivity caused by the movement of their own charge carriers, called *intrinsic.*

Formation of electron-hole pair is called *the generation of charge carriers.* This generation is possible in the case if electron energy exceeds E_g the band gap; in this case, the electron passes from the valence band to the conduction band (i.e. leaves the potential well of their intrinsic atom and detached from it); in the valence band formed hole. Thus, the band gap is the minimum energy that must be expended in order to snatch an electron from the covalent bonding. Note that if the electron energy does not exceed E_g, the formation of an electrically neutral bounding pairs of electron – hole, called *an exciton.* The excitons can play a significant role, for example, in the formation of color centers in alkali halide crystals.

In ideal crystal the concentration of electrons and holes are equal and grow with the increasing the number of violations of covalent bondings.

At the same time due to the presence of impurities and structural imperfections in the band gap can be present levels allowed for electron energies. These levels can be occupied by electrons or remain vacant. If the electron passes from the valence band to the allowed vacant level in bandgap or from occupied level to the conduction band, then occur generation of extrinsic charge carriers.

Extrinsic carriers. Sources of extrinsic charge carriers are electrically active impurity atoms. They may be atoms of elements constituting with semiconductor substitutional or implantation solid solutions and have a valence different from the valence basic atoms. Impurity atoms are divided into:

- *donors,* which gives excess electrons, because they have a high valence;
- *acceptors,* exciting valence electrons of the basic substance, as they have lower valence;

Donors created in semiconductor electronic conductivity (n-type conductivity), acceptors created – hole conductivity (p-type conductivity). Appropriate semiconductors called *electronic* (n-type) and *hole* (p-type). For elementary semiconductors (Si, Ge) donor is V group impurity atoms (P, As, Sb), while III group (B, Al, Ga, In) is acceptor. Donor and acceptor impurities called *dopants.* Doping- is the creation of semiconductor with predetermined conductivity type by introducing into its composition dopants. Arsenic atom has five valence electrons, atom of silicon – four, i.e. one electron of arsenic is not participate in the formation of covalent bonding. It is associated with its atomic strength of Coulomb interaction, which energy is comparable at room temperature with the energy of thermal motion (kT ~ 0,03eV). Therefore, the fifth electron of arsenic is easily detached from their atoms and become free, while the atom – a positively charged ion.

Creating of semiconductor with certain type of conductivity is very important, since the principle of many semiconductor devices action based on the impurity conductivity.

As for the ionization of both donor and acceptor impurities require energy, less than needed to break covalent bonding, that is, to form their intrinsic carriers ($E_{ext}<E_{int}$), the electrical conductivity of semiconductors n- and p-type, respectively, determined by the electrons and holes produced by ionization of the impurity. Such carriers are called *majority carriers.* In semiconductor of n-type majority carriers are electrons, non- majority – are holes; in the p-type semiconductor, on the contrary, the majority carriers – are holes, and non- majority – are electrons.

Along with generation of charge carriers in semiconductor, also occur *recombination* processes in which electrons from the conduction band returned to the valence band, resulting in the disappearance of electron – hole pair. The lifetime of carrier from its generation to recombination called *lifetime.* Respectively the lifetime of the electron is τ_n and hole is τ_p

$$\tau_n \sim 1/(p\upsilon_n),\ \tau_p \sim 1/(n\upsilon_p) \qquad (1.23)$$

where *n, p* – concentration of electrons and holes; υ_n, υ_p – the velocity of the motion of electron relative to the hole and respectively hole relative to the electron.

In real semiconductors lifetime of free carriers is 10^{-2} – 10^{-8} s, and for the stable operation of semiconductor devices it must not be less than 10^{-5}s.

The distance that the carrier has time to go through during its lifetime, is called *the diffusion length.* The diffusion length of an electron L_n and hole L_p connected with the lifetime and diffusion coefficient of appropriate sign charge (D_n and D_p) by the expression:

$$L_n = \sqrt{D_n \tau_n}\ , \qquad L_p = \sqrt{D_p \tau_p} \tag{1.24}$$

The lifetime and diffusion length is greater in the case of less impurities and other defects in semiconductor.

The electrical conductivity of semiconductors

In the absence of an external electric field, the electrons and holes make the chaotic motion through the crystal of semiconductor. When an external electric field is applied, electrons move against the field, the holes – in the direction of the field. The positively charged ions and negatively charged ions of acceptor impurity are immobile and do not participate in conductivity, because they are the structural elements of crystal lattice, which localized in its sites or in interstices.

In intrinsic semiconductor the concentration of free charge carriers (electrons and holes) is the same. Its conductivity is determined by the formula

$$\gamma_{\mathrm{int}}=\gamma_{\mathrm{n}}+\gamma_{\mathrm{p}}=\mathrm{neu_n}+\mathrm{peu_p} \tag{1.25}$$

Where $\gamma_{п}$, γ_{p} – conductivity respectively due to electrons and holes,; u_n, u_p the mobility of electrons and holes; e – electron charge.

The conductivity of the extrinsic semiconductor consists of intrinsic and extrinsic:

$$\gamma=\gamma_{\mathrm{int}}+\gamma_{\mathrm{ext}} \tag{1.26}$$

where $\gamma_{\mathrm{ext}}=n_neu_n$ for electron and $\gamma_{\mathrm{ext}}=n_peu_p$ for hole semiconductor; n_n, n_p – concentration of free electrons and holes formed respectively during ionization of donor and acceptor impurities.

Thus, the conductivity of the electron semiconductor is given by:

$$\gamma_n=n_neu_n+neu_n+peu_p=(n_p+n)eu_n+peu_p,$$

for hole semiconductor:

$$\gamma_p = p_p e u_p + n e u_n + p e u_p = (p_p + p) e u_p + n e u_n \qquad (1.27)$$

The electrical conductivity of the semiconductor is determined by the concentration of free carriers and their mobility. In turn, either concentration or mobility of free charge carriers depends on the temperature. In real semiconductor placed into the electric field, occur scattering of free charge carriers mainly on impurity ions and phonon: scattering on impurity ions predominates at low temperatures, and on phonons – at high temperatures. As a result of scattering, the carrier mobility decreases.

Temperature dependence of the electrical conductivity of semiconductors is exponential:

$$\gamma_{int} = const \cdot \exp(-E/2kT), \ \gamma_{ext} = \mathrm{const} \cdot \exp(-E/2kT) \qquad (1.28)$$

where Eext – ionization energy of impurities (respectively E_g or E_a).

At low temperatures the electrical conductivity due to the impurity charge carriers ($\gamma_{int} < \gamma_{ext}$), as $E_{ext} < E_g$. With increasing temperature γ_{int} increases and exceeds γ_{ext}. The temperature threshold at which $\gamma_{int} > \gamma_{ext}$, increases with increasing E_g.

Under the influence of the temperature difference in semiconductor changed charge carrier concentration and occur thermoelectric power, much greater in magnitude than in metals. Application of semiconductor converters of thermal energy into electrical energy based on this property.

To the magnitude of conductivity influence not only the temperature variation, but also other energy factors. Such effects are used for the creation of semiconductor converters (Table 1.2).

Table 1.2. Effects in semiconductors at external influences and the basic types of devices which operation is based on these effects

External action	Applied effect	Device
Electric field (E)	Conductivity Gunn effect	Resistor Gunn Generator

	Non-linearity of VAC of the $p - n$ junction Tunneling effect Radiative recombination of carriers	Rectifier, varistor Tunnel diode Injection laser Electroluminescent device
Light	Transmission of light with Certain frequency Generation of carriers Photovoltage	Optical filter Semiconductor laser Solar cell, solar battery
Electron beam	Generation of carriers	Semiconductor laser
Temperature (T)	ThermoEMF	Thermocouple, Thermogenerator
Light and E	Photoconductivity Generation of carriers	Photoresistor Photodiode
T and E	Dependence of γ from T	Thermoresistor
Pressure (p) and E	Dependence of γ from p	Strain sensor
Magnetic field (H) and E	Dependence of γ from H Hall Effect	Resistor, controlled by magnetic field Hall Sensor

The electron-hole junction (*p-n* – junction). Semiconductor layer between p – and n – regions in which occur change of conductivity type, called the *p – n* junction. Since in *n*-region electron concentration is much higher than the concentration of holes, electrons diffuse into the *p*-region and there recombine with holes. For the same reason from *p*-type region, to the *n*- region occur diffusion and recombination of holes with electrons.

Upon completion of these processes in the *p*- region remain negatively charged acceptor ions, while in the *n*-region – the positively charged donor ions, and at the interface of *p*- and *n* – regions formed double layer of spatial charge- negative charges in the *p*- region and positive – in *n*-region. This layer will be depleted by free charge carriers.

Uncompensated impurity ions in the boundary layer creates potential barrier (contact field), which can be overcome only by carriers that have sufficient energy and counter flows of which in dynamic equilibrium.

In the absence of an external electric field the total current through *p-n*- junction equals to zero. Upon application of field, the barrier height is changed and disrupted the balance of counter streams of carriers passing through it.

If to the *p*- region applied positive potential (direct offset), the barrier height is reduced, and an with increasing voltage (U) increases the flow of major carriers that can overcome the barrier; the flow of minority carriers is not changed. The total current through the *p-n* –junction (right branch of current-voltage curve, Fig. 1.3) is called *forward current* of *p-n* –junction, defined by the equation:

$$I \sim \exp\ eU/kT \tag{1.29}$$

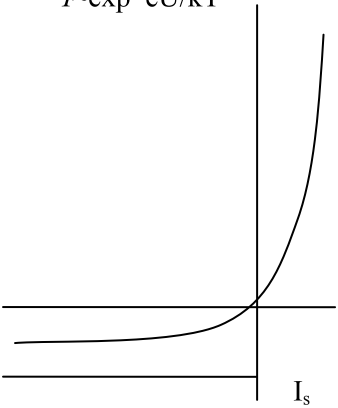


Figure 1.3 – Current-voltage curve of p-n junction

When the polarity of the external field (reverse bias) changed, the barrier height increases, the current through the *p-n* – junction is determined only by the diffusion of minority carriers, its value is small and independent of the applied voltage. Such current (I_s) called reverse current of *p-n*-junction or saturation current (left branch of the current-voltage curve, Figure 1.3).

The sign of U through the *p* – *n*- junction may vary by 5–6 orders of magnitude. Applying of *p* – *n*- junction based on this property for rectifying an alternating current (semiconductor diode).

The concentration of the minority carriers and hence the saturation current depends on external factors (thermal, optical, mechanical) that allows to create on the basis of the $p-n$- junction temperature, radiation, pressure detectors, as well as converters of various types of energies into electrical energy.

On the basis of $p-n$- junctions or by using them also created transistors, voltage regulators, amplifiers and generators, LEDs, semiconductor lasers, integrated circuits, etc. Formation of $p-n$- junction occurs at the contact of two semiconductors with different types of conductivity or doping of one part of semiconductor by donor and other part by acceptor impurity.

Important technical applications have *heterojunctions*, which was formed in contact:

- semiconductor with one type of conductivity, but with different value;
- metal and semiconductor;
- metal, dielectric and semiconductor.

Electrical properties of dielectrics

Conductivity of the solid dielectric with ionic structure is mainly due to the movement of ions. At low temperatures, weakly bond impurity ions move, while at high move also ions of the crystal lattice. The conductivity of dielectrics having an atomic or molecular lattice, which determined only by the movement of impurity ions. Their conductivity significantly lower than in materials with ionic structure.

In solid dielectrics are two types of conductivity:

- specific volumetric conductivity $\gamma_v=1/p_v$, Ohm^{-1}• m^{-1};
- specific surface conductivity $\gamma_S=1/p_S$, Ohm^{-1}.

Bulk conductivity (p_V) determines whether the current flow through the thickness of material. It is measured in Ohm • m. Surface electrical resistivity (p_S) determines whether the current flow on the surface. It describes the state of the dielectric surface layer (wetting or pollution) and measured in Ohm.

Insulation resistance is defined as the net of two resistances – volume and surface included parallel to each other:

$$R_{\text{ins}}=R_V R_S/(R_V+R_S) \qquad (1.30)$$

For body with constant cross-section S and length l the volume resistivity is determined by formula:

$$R_V = p_V l/S \tag{1.31}$$

from which:

$$p_V = R_V S/l \tag{1.32}$$

Specific surface resistivity is numerically equal to the square of resistance, on the surface of the selected material, in the case if current flows through two opposite sides of the square. Specific surface resistivity is calculated by the formula

$$\rho_S = R_S d/l \tag{1.33}$$

where d –width of the parallel set of electrodes; l – the distance between them.

Specific volume electric conductivity is expressed by the famous formula:

$$\gamma_V = nuq \tag{1.34}$$

where n, u, q – respectively, the concentration, the mobility, the charge of free ions.

The value γ_V stored in exponential dependence from temperature (since n and u depends exponentially on temperature):

$$\gamma_V = A\exp\left(-\frac{W}{\kappa T}\right) \tag{1.35}$$

where W – activation energy of conductivity ; A – constant of the material.

Since carriers are both intrinsic and extrinsic ions with energies of activation W_{int} and W_{ext} then

$$\gamma_V = A_1\exp\left(-\frac{W_{\text{int}}}{\kappa T}\right) + A_2\exp\left(-\frac{W_{ext}}{\kappa T}\right) \tag{1.36}$$

To this formula corresponds linear dependence of lnγ_V from the reciprocal temperature (1/T) (Figure 1.4).

High temperature area (left knee) corresponds to the area of intrinsic conductivity, while low temperature to the extrinsic conductivity. The angles of slop of straight sections to the axis of abscissa allows to determine the activation energy of charge carriers and conductivity type (intrinsic or extrinsic), and the intercept on the axis of abscissa is the extension of these areas – areas the temperature ranges of intrinsic and extrinsic conductivity.

Figure 1.4.– The temperature dependence of specific volume electrical conductivity of dielectric

In engineering calculations are often used formula ρ =B exp$\frac{b}{T}$, where B and b- constant of material.

And b constant equal to $\alpha_\rho = TK_\rho$ (K^{-1}), the electrical resistance. In dielectrics with crystal structure the electric conductivity varies in different crystallographic directions. The electrical conductivity of materials with *ionic lattice,* in some cases depending on the valence of its constituent ions. For example, lower valence may correspond to higher conductivity.

The specific electrical conductivity of *amorphous* dielectrics similar in all directions, due to the material composition and presence of impurities. In the *high molecular* compounds, it also depends on the presence of cross-linking between macromolecules and thus from the degree of polymerization and polarity of the material. Lowest electrical conductivity observed in the non-polar dielectrics.

When the voltage of the applied field increase conductivity of dielectrics increases significantly due to occurrence of additional electronic conductivity nature that at high values of E can lead to the breakdown. In this case $\gamma = \exp\sqrt{E}$. Character of changing of ρ_s and ρ_υ in dependence from various factors are generally similar, but the moisture and surface contamination reduces stronger ρ_s , than ρ_υ. Therefore, for increasing ρ_υ use polishing, cleaning and drying of the surface, and also applying to it varnishes, coatings and other hydrophobic coatings with high value of ρ_s .

In fact, the process of electrical conductivity in dielectrics is more complex, since the contribution made by the polarization currents.

§ 3. Optical properties

The optical properties are properties related to the generation, detection and interaction with the environment of optical irradiation that is electromagnetic waves in ultraviolet, visible and infrared range.

On this interaction is based different applications of optical radiation in the scientific, technical and practical reasons, in particular in electronics (optoelectronics, laser technology, etc.).

Optical spectra arise during quantum transitions between the energy levels of atoms, molecules, solids, liquids and gases. The emission spectra correspond quantum transitions from the upper to lower levels, while the absorption spectra – from the lower to the upper levels.

The spectra arising from quantum transitions between electronic energy levels in the atoms are called *linear.* The spectra resulting in molecules during transitions between electronic, vibrational and rotational levels are called *banded.* In the case of occurring thermal radiation of solid, liquid and gaseous bodies corresponds *continuous* spectrum. The higher the temperature, the shorter wavelength corresponds maximum position of such spectrum.

Different wavelengths **λ** and oscillations frequency **ν** corresponds different photon energy of photons hν, which equal to the energy difference of levels between of which occur the transition:

$$h\nu = \boldsymbol{\varepsilon_1 - \varepsilon_2} \qquad (1.37)$$

In Table 1.3. given value of ranges λ, ν, hν and temperature T, that characterized energy of photons (hν = κT) for three types of optical irradiation.

Table 1.3. Characteristics of the types of optical irradiation

Irradiation	λ, μm	ν, s^{-1}	hν, eV	T, K
infrared	10^3 – 0,74	$3*10^{11}$ – $4,0*10^{14}$	$1,25*10^{-3}$ – 1,7	14 – $2,0*10^4$
visible	0,74 – 0,40	$4*10^{14}$ – $7,5*10^{14}$	1,7 – 3,1	$2,0*10^4$– $3,6*10^7$
ultraviolet	0,40 –10^{-3}	$7,5*10^{14}$– $3,0*10^{16}$	3,1 – 125	$3,6*10^7$ – $1,0*10^{10}$

With the passage of the optical irradiation through substance (Wednesday) takes effect of its absorption – decreasing in the intensity of irradiation by law of Bouguer – Lamberg:

$$I = I_0 \exp\left(-k_\lambda, l\right) \qquad (1.38)$$

Where I_0 – intensity of incident light, *l* – the thickness of the absorbing medium, k_λ – absorption coefficient, which depends on λ and the nature of substance medium.

Dependence of k_λ from λ is called the *absorption spectrum* of substance. The absorption spectrum of isolated atoms has the form of narrow lines, that is necessary on narrow range of wavelengths (hundredths – thousandths of nanometer). The spectrum of molecules, determined by the frequency of their oscillations, have a wide range of wavelengths (few tenths of – hundreds of nanometers), the spectrum of solids – a very wide range (hundreds or thousands of nanometers). The latter is consequence of the energy transferred by irradiation of one particle, quickly transferred to the solid with collection of particles.

The process of absorption of the irradiation associated with the transition of electrons in atoms, ions, molecules of absorbing bodies from lower energy levels to higher, i.e. with a transition of particles to excited state.

The light beam with not very high intensity I_0, k_λ does not depend on I. But if the initial intensity is very large, then a large proportion of absorbing particles going into an excited state and staying in it relatively long time, lose the ability to absorb further irradiation. Under these conditions k_λ becomes function of intensity. There comes *a nonlinear absorption of light.*

The reverse transition of atoms, molecules from the excited state to unexcited associated with *luminescence.* Under luminescence understand irradiation, excessive above heat. Luminescence is inherent in all three ranges of irradiation.

By type of excitation distinguish *photo, radio and electro-luminescence,* which corresponds to the excitation by light, ionizing radiation of all kinds, electric field.

Necessary condition of luminescence is the presence of discrete energy spectrum. Therefore metals, which are characterized by continuous energetic spectrum of valence electrons do not luminesce.

The study of the physical parameters of the light absorption (irradiation) and luminescence provides get information about the energy state of matter, impurity band structure of semiconductors, to detect small amounts of impurities, etc.

Important optical phenomena and characteristics include *polarization, diffraction, refraction and reflection of light, transparent environment.*

On the quantum positions polarization of light associated with the same spin state of all photons that form light flow. A lot of kinds of full and partial polarization is existed. They occur in different physical effects – in the case of passing through an anisotropic medium, double refraction, diffraction on ultrasound, strong magnetic and electric fields (magneto and electro-optics), reflection and refraction of light, resulting in different absorption coefficients for different polarizations. Laser irradiation is the most polarized type.

Various types of effects on the light polarization are basis of the use of this phenomenon for the diagnosis of optically anisotropic crystals and media, staining polarized beam of white, crystal-chemical study and magnetic structure of solids, the study stresses in transparent media.

Distribution of powerful light beams, such as laser, and their interaction with matter not only change the law that describes the absorption and other optical characteristics of the medium, staining of polarized white beam, the study of crystal-chemical and magnetic structure of solids, investigation of stresses in transparent media.

Distribution of powerful light beams, such as laser, and their interaction with matter not only change the law that describes the absorption, but also other optical characteristics of medium, in particular nonlinear, which has dependence to strength of the field **E** are polarized and many other optical phenomena and processes.

Using infrared lasers led to the discovery of the nonlinear behavior of charge carriers in semiconductors, which does not appear in the visible wavelength range.

With the interaction of optical irradiation with the medium associated phenomena of reflection and refraction. In the fall of rays from the first medium to the interface with the second arises irradiation propagating from the boundary back into the first medium. The nature of reflection influence the size of irregularities at the interface and the degree of ordering in their arrangement.

If irregularities are small compared with the wavelength $\boldsymbol{\lambda}$, then took place mirror reflection. If they are comparable or irregularities size greater than λ (rough surface) and irregularities arranged randomly, then reflection has diffuse (scattered) character. If irregularities are arranged orderly, then the character of reflection is close to reflection of lattice diffraction. Reflection is accompanied by the refraction of light.

An important characteristic of the medium used in the diagnosis of many materials, including semiconductors, is *transparency. Transparency is the ratio of radiation flux transmitted without changing the direction of path equal to one to the stream included in this medium as parallel beam.* Transparency depends on the wavelength of the irradiation.

Many substances that are transparent in visible light, are opaque to infrared radiation (IR), and vice versa. Plates of silicon and germanium, are not transparent in the visible range, are transparent to infrared radiation (germanium for $\lambda > 1{,}8$ μm, silicon $\lambda > 1{,}0$ μm).

Various characteristics of optical irradiation – the intensity, frequency of phase, polarization, and others can change the time according to given law. Light modulation can be carried out in various ways, e.g., by using various types of mechanical breakers. The most interesting and gives possibility of using physical effects – electro-optical, magneto-optical, elasto-optical accompanying the propagation of light streams in different conditions and environments.

§ 4. Acoustic properties

Acoustic properties are properties associated with the generation, detection, and various kinds of interaction with the medium of elastic vibrations and waves of very low frequency (from 0 Hz) to extremely high ($10^{11} – 10^{12}$ Hz).

The frequency range from 16 Hz to 20 kHz detected by the human ear, the range below 16 Hz is infrasound, above 20 kHz – ultrasound, high frequency range $10^{12} – 10^{13}$ Hz – hypersonic.

A special case of acoustic waves are surface acoustic wave (SAW). These waves propagate along the free surface of solid or along the borders of solid with other media. At distance from the border, these waves are damped.

SAW can be in two types:

1) with vertical polarization, when the elastic vibrations of the medium particles under the influence of SAW occur in the vertical border of plane;

2) with horizontal polarization when these fluctuations are parallel to boundary and perpendicular to direction of the wave propagation.

Elastic acoustic waves are generated by any phenomena caused by local changes in pressure or mechanical stress. Different sources generate acoustic waves of different frequencies.

Acoustic wave propagation is characterized by the speed of sound $\mathbf{c_s}$. The speed of sound is very small compared with the speed of optical irradiation (light). It depends on the aggregation state and nature of the material: $\mathbf{c_s}$. in gases less than in liquids, and in liquids less than in solids. In Table 1.4. given the values of sound speed for some substances.

In isotropic solids c_s depends on the elastic moduli, in anisotropic solids speed of sound is anisotropic. In piezoelectric and ferroelectrics c_s depends not only on the elastic moduli, but also on the piezoelectric coefficients and the strength of electric field, while in ferromagnetics – from the strength of magnetic field.

Table 1.4. Speed of sound in some substances

№	substance	speed of sound c_s, m/s
1	Air	331
2	Hydrogen	1284
3	Water	1490
4	Mercury	1453
5	Gold	3200
6	Glasses	3760 – 4800
7	Iron	5900
8	Fused quartz	5970
9	Aluminium alloys	6000

Measurement of c_s is used to determine the elastic moduli of solids, the Debye temperature for the investigation of the band structure of semiconductors, the definition of the Fermi level in metals and others.

In the propagation of sound wave occur absorption of sound, which much weaker than the absorption of the optical irradiation. Absorption is associated with the transition of the sound wave energy into other forms of energy, mainly in the heat. The consequence of this absorption is sound attenuation, i.e. reduction of its intensity and amplitude.

In the propagation of acoustic waves of high intensity (amplitude) as the passage of the optical radiation of high intensity, take place phenomenon of nonlinearity. This diffraction of waves and scattering of sound become dependent not only on the frequency and speed of sound wave, in linear acoustics, but also to the amplitude of wave, sinusoidal wave is distorted, occur sound pressure of irradiation, etc.

The effect of non-linearity due to the fact that the propagation of acoustic waves of high intensity changes the properties of the medium itself, which affects both the propagation of the waves and other disturbances.

Interaction of acoustic waves with electrons have particular importance in electronics and called *acoustic-electronic interaction* (AEI), while interaction with electronic waves called *acoustic-optical interaction* (AOI).

AEI manifests itself in the ultrasonic and hypersonic vibrations with frequency 10^7 – 10^{13} Hz, when under the influence of propagating acoustic wave occur elastic deformation of the crystal lattice and changing its intracrystalline field. The energy and momentum of ultrasonic and hypersonic waves transmitted by conduction electrons (particular case of the electron-phonon interaction).

The transfer of energy results to additional electronic absorption of sound and heating of the electron gas, while transfer of momentum $\frac{h\omega}{c}$ – to the emergence of current or e.m.f. in metal or in semiconductor *(acoustic-electric effect)* in the direction of sound propagation (entrainment effect). In addition to changes in the electrical conductivity, AEI changes the heat and thermal conductivity.

AEI mechanism is different for crystals of different nature. In ionic crystals and metals have the ionic interaction – acoustic wave displaces the ions from their equilibrium position, occur ionic current and field, which acting to conduction electrons.

In number of semiconductors (Ge. Si) and semimetals (Bi, Sb, As) realized the potential – deformation interaction – under interaction of ultrasonic wave changes the bandgap, occur regions with lower and higher charge density acting on the conduction electrons.

In piezoelectric semiconductor of $A^{II}B^{VI}$ (CdS, CdSe, ZnS, ZnO), $A^{III}B^{V}$ (InSb, GaAs) and in others manifest piezoelectric interaction – the deformation of these crystals is accompanied by occurring of electric field and vice versa.

From the mechanism of AEI depends magnitude of the electronic absorption of ultrasonic waves. It is maximal in piezoelectrics. In metals and in conventional semiconductors electron absorption becomes noticeable only at low (helium) temperatures.

The transfer of ultrasonic wave impulse by conduction electrons leads to *acoustic- electric current.* If to the crystal applied also constant external electric field E, which creates electron drift in the direction of the ultrasonic wave, then AEI depends essentially on the drift velocity $\mathbf{v_{dr}}$ and propagation velocity of sound $\mathbf{c_s}$. When $v_{dr} < c_s$ ultrasonic wave is absorbed by the electron gas at $v_{dr} > c_s$ electrons give their kinetic energy to ultrasonic wave, occur strengthening (increasing of amplitude). This increase has practical interest for the surface acoustic waves.

AEI leads to number of non-linear acoustic effects, is particularly noticeable in piezoelectric materials used in acoustic electronics, in memory elements.

Most of the acoustic-optic device works on the phenomenon of light diffraction by ultrasonic waves.

Elastic deformation in the sound wave leads to periodic change in the refractive index n of the medium. As a result, in the medium occur structure similar to diffraction lattice having period equal to the wavelength of sound $\boldsymbol{\lambda_s}$. If at such medium distribute light beam, the medium will have diffraction light beams. Their characteristics – direction in space, polarization, intensity – depends on the sound field parameters **(γ, I)** and the angle θ, at which the light falls on the acoustic beam.

The frequency of the diffracted light is different from the frequency of the incident light on magnitude of the sound frequency. At the exit of the acoustic beam light wave is modulated in phase and deviate from direction.

Interaction of sound waves in solids and liquids with optical irradiation is effectively used in electronics, laser technology, optics to control the amplitude, polarization, spectral composition and direction of propagation of the optical beam.

With the help of the diffraction of light by ultrasonic waves are determined by the characteristics of the sound field, absorption, and the speed of sound, elastic modulus of elastic-optical and magnetic-optical materials, created apparatus for receiving signals in ultrasonic delay lines.

In interaction, which propagate in the crystal of ultrasonic and hypersonic waves with frequency from 10 mHz to 1.5 GHz with each other and with electrons, as well as application of surface acoustoelectronic devices based on acoustic waves for the conversion and processing of electrical signals.

§ 5. Magnetic properties

The substances have magnetic properties due to the magnetic moment occur because of the motion of electrons (the magnetic moments of the atomic nuclei approximately thousand times smaller than the magnetic moments of electron).

There are two main types of electrons motion, leading to the appearance of magnetic moments: orbital (orbit around the nucleus) and spin (on its axis). Accordingly, there are the orbital and spin magnetic moments.

Spin magnetic moment equal to one Bohr magneton, J/T:

$$M_{m\,sp} = \frac{|e|}{2m}\frac{h}{2\pi} = 9{,}273 * 10^{-24} \qquad (1.39)$$

where e, m – charge and mass of the electron.

In addition to these two main types of electrons motion, there is another, which is manifested in the application of an external magnetic field. In this case, an electron moving in closed orbit, changes its trajectory: instead linear it becomes spiral.

By its nature existed following types of magnetism: diamagnetism, paramagnetism, ferromagnetism, antiferromagnetism and ferrimagnetism. In Figure 1.5. shown the orientation of the magnetic moments.

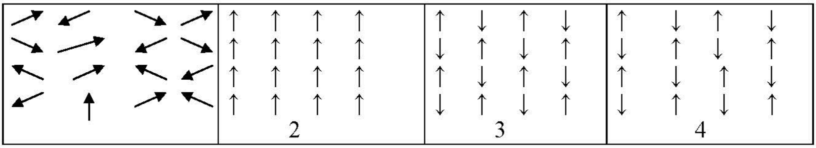


Figure 1.5. – Orientation of the magnetic moments of neighboring atoms at 0K in materials with different magnetic nature: 1 – paramagnetic; 2 – ferromagnet; 3 – antiferromagnetic; 4 – ferrimagnet

Let's talk about the main magnetic characteristics. *The magnetic moment of body* **M** equal to the product of the magnetization **J** on the body volume **V**:

$$\mathbf{M} = \mathbf{J}\,\mathbf{V} \tag{1.40}$$

The magnetization of the material – its ability to change its magnetic moment under external magnetic field strength H is characterized by magnetic susceptibility æ:

$$J = æ\,H \tag{1.41}$$

The resultant magnetic field in the material known as *magnetic induction* B. The value of **B** is associated with the strength of external magnetic field H and magnetization of the substance J by relation:

$$B = H + 4\pi\,J \tag{1.42}$$

The ability of substance to change its induction B in under the influence of the external field H is characterized by permeability μ:

$$B = \mu H \tag{1.43}$$

Dependence of J, and B, and therefore, μ from H are nonlinear. The limit value of μ when strength H tends to zero, called *the initial magnetic permeability* μ_i.

Magnetic permeability is related with the magnetic susceptibility by ratio:

$$M = 4\pi\,æ + 1 \tag{1.44}$$

The physical nature of *diamagnetism* is associated with the rotation of spiral electron by closed orbits induced by the external field and gives rise to undamped eddy microcurrents. Internal magnetization arises in the body under the influence of an external magnetic field and directed toward the field, so the diamagnetic susceptibility $æ_{mD}$ has negative value.

The main contribution to diamagnetism of atom make outer electrons. Diamagnetism enjoyed all substances without exception.

But the prevailing type of magnetism occur only in substances with filled electron shells: inert gases, Na^+, Cl^-type ions, semiconductors (germanium, silicon, selenium, etc.).

If substances along with diamagnetism have other kinds of magnetism, then role of the latter covers the role of diamagnetism. The diamagnetic susceptibility of the solids are in order of $10^{-5} – 10^{-6}$ Gs/E (Gauss to oersted).

Under *paramagnetism* understands the property of body to magnetize in external field H in the direction of the field. Consequently, the paramagnetic susceptibility has positive value. Therefore paramagnetic bodies are attracted to the poles of the magnet, while diamagnetic and repelled. The total magnetization of paramagnetics equal to the sum of external and internal fields.

The main feature of the paramagnetic bodies is that they have their own magnetic moments of the atoms (orbital and spin), but due to the interatomic interaction magnetic orbital angular moments of two paired electrons canceled each other. In the result all filled electron shells and orbitals have zero orbital magnetic moment, and did not contribute to the paramagnetic properties. Paramagnetism is found only on the unpaired valence electrons – the conduction electrons.

Spin moments do not experience such interaction of the crystal field, and therefore their contribution to the magnetic moment of atoms in solids is significant.

In the absence of external field, the magnetic moments of atoms due to thermal motion oriented randomly, causing the magnetization of paramagnetics under these conditions is equal to zero. This is difference from ferromagnetics.

When an external magnetic field H applied moments of atoms predominantly oriented along the field. With increasing H magnetization of paramagnetic increases by law $J=æ_{mp}H$, where $æ_{mp}$– magnetic susceptibility of 1 cm^3 substance (for paramagnetics æ is equal to $10^7 – 10^{-4}$). If the field H is very large, all magnetic moments are oriented along the field, occur magnetic saturation.

With increasing temperature at constant H increases disorienting effect of thermal motion.

The substances in which no conductive electrons, magnetic moments of electron shells of atoms compensated and magnetic moment has only nucleus. The paramagnetism of such substances is very small (10^{-9} – 10^{-12}) and can be observed only at very low temperatures (T = 0.1 K).

Nuclear paramagnetism in the absence of strong interaction between the spins of nuclei and electron shells of atoms characterized by the value

$$æ_{mn}=\frac{NM_{mn}}{3kT} \qquad (1.45)$$

where M_{mn} – magnetic moment of nucleus equals approximately to 0,001 of the magnetic moment of electron, from which $æ_{mn} \approx 10^{-6}\ æ_{me}$.

Research of paramagnetic properties with using electron paramagnetic resonance (EPR) and nuclear magnetic resonance (NMR) allows to determine the magnetic moments of the individual atoms, ions, molecules, nuclei, to study the structure of individual molecules and complexes, to carry out thin structural analysis of materials.

For this purpose used the sharp demagnetized paramagnetics in thermal insulation conditions (adiabatically), in which the spins acquire random orientation, accompanied by decreasing in temperature *(magnetic cooling).*

Ferromagnetism as paramagnetism associated with the spin magnetic moments of electrons. But in contrast to the paramagnetics in ferromagnetics have separate microregions (domains), which below of certain temperature (Curie temperature T_c) spin moments of all atoms have the same orientation in the absence of external magnetic field. The domain is the microregion about micrometer, spontaneously magnetized to saturation at temperature below T_c.

In the absence of external field the magnetization vectors of different domains are oriented randomly and canceled out. When external magnetic field applied the magnetization vectors of all domains gradually reoriented along the field. Upon completion of this process (in fields N≈8 kA/m) achieved limit value of magnetization J_S and induction B_m. Value of J_S is maximal at T = 0K.

With increasing temperature J_S decreases and at T= T_c become equal to zero, the ferromagnetic transite to the paramagnetic state.

The emergence of domains due to the fact that the exchange interaction decreased the energy of neighboring atoms, but at the same time increased the amount of the total magnetic moment of ferromagnetic volume and magnetic- static energy (magnetic field, distribution to environment). Minimizing of total magnetic energy is achieved by splitting into domains.

For the spontaneous magnetization must honored the following two conditions:

1) the presence of uncompensated spins;

2) the ratio of the interatomic distance of neighboring atoms **a** to the diameter of electron subshell with uncompensated spins **d** must be within $\frac{a}{d}=2\div5$.

At ratio $\frac{a}{d}<2$ exchange interaction leads to anti-parallel arrangement of neighboring spins, i.e. to antiferromagnetism. At ratio $\frac{a}{d}>5$ exchange interaction within domain is reduced, ordering in spin orientation is absent. State of body will be paramagnetic.

In addition to the exchange interaction between the spins of neighboring atoms in the crystal take place interaction between the spins and the lattice atoms, because of which the total magnetic moment arranged along certain preferred crystallographic directions, called as the axes of easy magnetization: <100> for bcc, < 111> for the fcc and <0001> for г.к. The energy of the magnetic moments is minimal when they are oriented in the direction of easy magnetization.

The work done by external magnetic field to rotate the magnetization vector J_i from the light direction to hard direction of magnetization, called *the energy of magnetic anisotropy* E_{an}.

Domains with different orientation are separated from each other by transition region, in which the orientation of spins smoothly transite from one domain to another orientation. These transitional areas are very similar to the grain boundaries in polycrystalls. They have high energy, and tends to reduce the overall system energy to migrate towards the domain of higher energy, thereby reducing its volume.

The thickness of the border is usually smaller to one order than the size of domain. In thin magnetic films can be arrange orderly movement of domains and even individual fragments of the domain boundary, creating appropriate controlling magnetic field. This principle is implemented by storage devices with cylindrical magnetic domains (CMD memory), and number of magnetic-optical devices for controlling the light beam.

Among the most important characteristics of magnetic materials that define the field of application limiting form of the hysteresis loop. Ferromagnetics with narrow hysteresis loop and low coercitive force (H_c <2,4 ÷ 4,0 kA/m) are called *soft magnetic,* and with high value (H_c> 4.0 kA/m) – *magnetic solid.* If necessary, to maximally reduce the magnetic losses H_c can not exceed few tens of amperes per meter.

The magnetic interaction of electrons is also changing the interatomic distances and therefore the size and shape of the body – this phenomenon is called *magnetostriction.* This phenomenon is associated with change in the magnetic and exchange forces and difficult depending on the field strength, the electronic structure – valence electron, crystallographic direction, impurities and others. In ferromagnetics magnetostriction reaches significant values. Elongation in them may have value $\frac{\Delta l}{l} = 10^{-5} \div 10^{-3}$. The largest magnetostriction possess some rare earth metals. For example, in dysprosium $\frac{\Delta l}{l} \cong 1.2 * 10^{-3}$, which is 30 times larger than in nickel. Magnetostriction of different materials can vary not only the absolute value but also sign of size changes. Magnetostriction is widely used in ultrasonic generators, delay lines, and others. Do not confuse magnetostriction with another phenomena- *changing the magnetization of ferromagnetic body during deformation (magnetic-elastic effect).* Simultaneous exposure to deformation and magnetization can change the value of H_c, to facilitate or impede the magnetization, to change the shape of hysteresis loop.

In some solids exchange interaction of neighboring atom's electrons occur at certain temperature (below the Nel temperature T_N) antiparallel spin ordering, antiferromagnetism, in contrast to what occurs in ferromagnetics.

At temperatures above T_N substance is paramagnetic. Examples of antiferromagnetics is manganese oxide MnO.

Do not fully compensated antiferromagnetic ordering of the spin magnetic moments called *ferrimagnetism.* The most important ferrimagnetism are the ferrites- ionic compounds with general formula MFe_2O_4 (or $MO\ Fe_2O_3$), where M – metal.

The magnetic field strength H (A/m) proportional to the current flowing through the conductor. It can be calculated for infinitely long linear conductor by the formula $H=I/2\pi r$ and for toroid and for infinitely long solenoid $H=nI$, where r – distance from the conductor to the point where the field is measured, n-number of turns per unit length of the solenoid, I-current flowing through the conductor (A).

The magnetic moment M ($A \times m^2$). Any substance placed in magnetic field of strength H, magnetized and will have magnetic moment. Its value can be directly measure by magnetometer. Magnetic moment also has circular current: $M= IS$, where the S-the area of current.

The magnetization J (A/m) – the magnetic moment per unit volume $J=M/V$. The magnetization is related to the magnetic field strength by ratio $J = \chi_m H$, where χ_m – magnetic susceptibility – quantity characterizing the ability of substance to change the magnetic moment under external magnetic field. For vacuum $\chi_m = 0$.

The magnetic induction B (T) – the magnetic flux passing through unit area perpendicular to the force lines of uniform field, w2hich determined by the formula $B=\Phi/S=QR/S$, where Φ –flux, Q –is the number of electricity induced in circuit with resistance R, with $1T = 1kl \times ohm / m^2$.

Magnetization in external magnetic field body creates its own field. Relative magnetic permeability and magnetic susceptibility are related by $\mu = 1 +\chi_m$.

The classification of materials for their magnetic properties

According to the magnetic properties materials are divided into groups: 1) diamagnetic; 2) paramagnetic; 3) ferromagnetic; 4) anti-ferromagnetic; 5) ferrimagnetic.

The **diamagnetic** materials are magnetized in direction opposite to the external magnetic field. Magnetic susceptibility $\chi_m <<0$ (about $10^{-4} - 10^{-6}$). Diamagnetism is due to orbital magnetic moments and occurs when the number of electrons in the atom is even, that is, the spin moments are compensated. Outwardly, it appears in the ejection of matter from the field. Diamagnetic are Cu, Ag, Au, H_2O, etc.

Paramagnetic materials – substances which have the spin magnetic moments of the atoms that are not compensated (Fig. 1.4). At H=0, they are oriented randomly. In magnetic field ($H\neq0$) the magnetic moments tend to be oriented in the direction of the field. But this prevents the thermal motion of particles. Therefore, the magnetic susceptibility of paramagnetics depends on the temperature (Curie law) $\chi_m = \frac{C}{T}$, where C- Curie constant (for paramagnetic materials $\chi_m \sim 10^{-4} - 10^{-5}$). Since $\chi_m > 0$, paramagnetic drawn into the magnetic field. On the physical nature of the paramagnetism similar dipole relaxation polarization of dielectrics. Paramagnet under normal conditions are alkaline and some transition metals.

Ferromagnetic materials ($\chi_m >>0$ and up to several thousand) similar as paramagnetics have uncompensated spin moments (Fig. 1.4 (2)). In ferromagnetics, existed areas of spontaneous (inadvertent) magnetization, called *domains.* Each domain is magnetized to saturation, i.e., inside the magnetic moments of neighboring atoms are arranged in parallel through the parallel electron spins of unfilled shells. This is due to the *exchange interaction* of the electrons. The exchange interaction is implemented in the crystal lattice under overlap of the electron shells of neighboring atoms. The electron of one atom is partly owned by another. As result, the energy system will be different in the case of parallel and antiparallel orientation of the spins. The energy of the exchange interaction is given by $E_{exch} = -2As_1s_2\cos\varphi$, where s_1, s_2 – the resulting spins of the atoms, φ – the angle between the vectors of this spins, A– constant of exchange interaction (is the energy difference between two electrons with parallel and antiparallel spin orientation).

If A> 0, E_{exch} is minimum at $\varphi=0$, in the case of parallel orientation of the spins. In this case, the material is ferromagnetic.

If A <0, E_{exch} is minimum at φ =180, i.e., when antiparallel orientation of the spins, material is antiferromagnetic.

Constant of exchange interaction depends on the distance between neighboring atoms in the crystal lattice.

Ferromagnetic materials include: Fe, Ni, Co; rare earths elements; alloys of magnetic elements; alloys on the basis of non-magnetic elementsv (e.g. alloys on the basis of Mn).

Antiferromagnetic materials are characterized by antiparallel orientation of the spins of neighboring atoms. Antiferromagnetic crystal lattice can be viewed as consisting of two sublattices with opposite spin orientation. The total magnetic moments of the sublattices are compensated, and at H=0 J=0. Antiferromagnets are Mn, Cr, NiO, MnO, Fe_2O_3 and etc.

Ferrimagnetic materials can be represented as antiferromagnets with uncompensated magnetic moments of the sublattices. At H=0 J≠0, material as well as ferromagnetic spontaneously magnetized. Ferrimagnetics include ferrites, some dielectrics and semiconductors.

The domain structure of ferromagnetics

Domain – region of ferromagnetic magnetized to saturation in the direction of easy magnetization. The size, form of domain and location of boundaries between them are determined by the condition of minimum free energy of the crystal.

Single-domain state is energetically non-advantageous, since the ends of the ferromagnetic become poles, which creating demagnetizing field, that corresponds to free energy.

During dual domain structure of the crystal free energy is significantly reduced, with further fragmentation reduced even more.

The most energetically favorable is structure with closure domains, in which the free energy tends to minimum, since all the magnetic fluxes are closed inside the crystal.

The domain width is 10^{-3}-10^{-1} mm. At length, they may extend from one end of the crystal or grain to another, and even move from grain to grain.

The material layer separating two adjacent domain called domain walls or wharf. Within it there gradual change in the orientation of the magnetic moment from one direction to another.

Within it occur is gradual change in the orientation of magnetic moment from one direction to another.

Ferrimagnetics have similar domain structure.

Magnetic anisotropy

In ferromagnetic crystals exist light direction (LDM) and the hard magnetization (HDM). At H=0 vector of magnetic moment is oriented along the domain of LDM.

Iron having BCC lattice, LDM coincides with the edge of cube <100>. In this direction, the magnetization reaches saturation in weak fields. The spatial diagonal of cube <111> is HDM.

In nickel, having FCC lattice, conversely, <111> – is LDM, <100> – is HDM.

The direction of easy magnetization in single crystal of cobalt coincides with the direction of hexagonal axis.

Magnetic anisotropy plays an important role in the process of magnetization. For improving the magnetic properties of certain materials in them created *crystallographic texture* in which crystal grains are oriented in the material so that LDM each of them coincides with the direction of external magnetic field.

Magnetic properties in alternating fields

In the alternating magnetic fields that occur when the winding passes alternating current with frequency of 50 Hz to tens of thousands of MHz, essential acquire two factors:

1) eddy currents created when the magnetic flux in the conducting medium;

2) increasing in phase shift between B and H (lagging B from H), which is due to the inertia of the magnetization process and reversal magnetization.

Eddy currents impede penetration of the field into the sample, so B inside of sample is lower than on its surface. This phenomenon is characterized by the penetration depth (Z), i.e. distance from the sample surface, which field amplitude is reduced by *e* relative to the surface. For efficient use of the material thickness (d) it is need to be $d \approx 2Z$. The higher the μ, the smaller the Z.

The dependence of magnetic properties to temperature

Thermal motion violates the parallel orientation of magnetic moments of atoms in the domain. At certain temperature Θ_c, which called the *Curie temperature,* the domain structure disappears and ferromagnetic transfer to paramagnetic state.

The higher E_{exch}, the more heat is required for violations of spontaneous magnetization, i.e., the higher Θ_c. Constant of exchange interaction A associated with Θ_c by relation $A \sim 2k\Theta_c$, where k- is Boltzmann's constant.

For μ characteristics change depending on temperature used temperature coefficient of magnetic permeability:

$$\alpha_\mu = \frac{\frac{1}{\mu} d\mu}{dT} \tag{1.46}$$

Temperature changes of the magnetic properties can be reversible or irreversible. Irreversible changes (magnetic aging) occur by process, that change the structure of the material, and reversible associated with changes in physical parameters.

§ 6. Thermal properties

The thermal conductivity. Under the thermal conductivity refers to the process of heat distribution from the hotter parts of the body to less heated, resulting in temperature equalization.

At thermal conductivity heat transferring occurs as result of energy transfer from the particles with higher energy to particles with less energy by direct contact of system's hot parts with cold.

The basic Law of thermal conductivity similar to the first law of diffusion that the density of heat flow Q is proportional to the temperature gradient

$$Q = -\frac{\chi dT}{dx} \tag{1.47}$$

where χ – thermal conductivity coefficient (W/cm*K) which depends on temperature, pressure, composition and structure of the material.

The minus sign means that the distribution of heat (heat flux) is opposite to the gradient.

In general case the thermal conductivity in solids carried out by two mechanisms – the movement of current carriers, mostly electrons, and elastic thermal vibrations of the lattice atoms. Consequently:

$$\chi_\Sigma = \chi_e + \chi_f \tag{1.48}$$

where χ_e – electronic and χ_f – lattice (phonons) components of the thermal conductivity.

The contribution of these components in dielectrics, metals and semiconductors – are different.

In dielectrics, which do not have free electric charges, the thermal conductivity due to the transfering of energy from the high-energy atoms and molecules to neighboring atoms and molecules having lower energy, i.e. transferring of thermal motion is carried out by phonons. The scattering of phonons by structural lattice defects and phonons hinders heat transfer. The thermal conductivity of dielectrics generally substantially lower than the thermal conductivity of conductors. Some inorganic dielectrics such as Al_3O_3, BeO, have thermal conductivity, commensurate with thermal conductivity of metals that explained by the electronic type of electro – and hence conduction.

For them, we have the following:

$$X_D = C\overline{\upsilon}\overline{l} \tag{1.49}$$

where C – thermal conductivity of dielectric, which coincides with the heat capacity of the phonon's "gas"; $\overline{\upsilon}$ – average speed of phonons, approximately equal to the speed of sound; $\overline{l}$ – average length of free path for phonons, depending on what happens the phonon scattering: on phonons, on crystal defects or on its outer edge.

In *metals,* characterized by high concentration of conduction electrons at normal temperatures $\chi_e >> \chi_f$ and contribution to the lattice of thermal conductivity can be ignored (except for the low temperature below 300 K).

During heat conduction process each electron transport in the presence of temperature gradient energy kT, so that the ratio of thermal conductivity to the electrical conductivity in wide range of relatively high temperatures is proportional to T (Wiedemann – Franz law):

$$\frac{\chi_M}{\sigma_M} = \frac{\chi_{\acute{Y}}}{\sigma} = (\frac{\pi^2}{3})(\frac{k}{e})^2 T \qquad (1.50)$$

As well, $\sigma \approx \frac{1}{T}$, and $\chi \approx \sigma T$, from dependence clear that at relatively high temperatures χ does not change with temperature.

With decreasing of temperature below 300 K, and respectively decrease in the velocity of electrons becomes noticeable contribution to the scattering of electrons by atomic vibrations and impurities and therefore at $T \leq 300$ K χ varies strongly and $\chi_e \approx T^2$.

In semiconductors, due to the low concentration of conduction electrons χ_e role is much smaller than in metals ($\chi_e < \chi_f$) and on the first place the lattice (phonons) component χ_f. Its role is greater, when the concentration of carriers is lower and respectively σ. For germanium and Bi_2Te_3semiconductor compound:

materials	σ, Sm/sm	χ_Σ, (W/(cm*K)	χ_e, (W/(cm*K)	χ_e, / χ_Σ
Ge (doped)	1	0,60	$6{,}6 \cdot 10^{-6}$	10^{-5}
Bi_2Te_3	10^3	$2{,}4 \cdot 10^{-2}$	$6{,}7 \cdot 10^{-3}$	0,28

This implies that the contribution χ_e to the thermal conductivity of Bi_2Te_3 considered, while in germanium can be neglected.

Depending on the purpose and conditions of working semiconductor devices, to the χ values of appropriate materials submitted different requirements. PCE of thermoelectric power converters is higher in the case of χ less value of thermoelectric materials. Substrates of microelectronic devices (integrated circuits) must have high values of χ, while thermoelectric sensors has low value, etc.

Thermal expansion (TE) – change (generally an increasing) in the size of body during heating process. Thermal expansion due to the anharmonicity of the thermal vibrations.

Typically, the thermal expansion is characterized by isobaric (at constant pressure P) volume coefficient (α_v) or linear – for solids (α_l) – thermal expansion (CTE):

$$\alpha_v = \frac{V_2 - V_1}{V(T_2 - T_1)}; \qquad \alpha_l = \frac{l_2 - l_1}{l(T_2 - T_1)}; \qquad (1.51)$$

where V_2, l_2 and V_1, l_1 – volume and length of the body along the chosen direction at T_2 and T_1 respectively ($T_2 > T_1$).

In general case, α_T is smaller when strength of interatomic bondings is greater.

In the table shown values of α_l for some materials used in semiconductor electronics.

materials	Al	Au	Mo	Ge	Si	α-Al_2O_3	GaAs
$\alpha_l \cdot 10^6$ K^{-1}	26	14	5	6,69	7,0	5,5	6,67

The thermoelectromotive force (TEMF) – electromotive force E that occurs in electrical circuit consisting of several different conductors, contacts between them have different temperatures (Seebeck effect). A circuit consisting of two different conductors, called as thermoelement or thermocouple.

The value of TEMF depends on the temperature of hot T_h and cold T_c junctions and on the conductor's material. In small temperature range (0 – 100 ° C) the value of $E=\alpha(T_h - T_c)$, where α – the coefficient of TEMF (Seebeck coefficient [μV/K]), depending on the material of both the conductor and temperature range.

At the following table shown values of α for various materials with respect to α of lead. The sign "+" means that current flows from the lead to the material (electrons are moving in the opposite direction), the symbol "-" shows that current flows from the material to lead.

№	metals	α, μV/K
1	antimony	+ 43
2	chromel	+ 24

3	bismuth	– 68
4	constantan	– 38
semiconductors		
1	$Bi_2Te_{2,4}Se_{0,6}$ (n–type)	– 175
2	$Bi_{0,52}Sb_{1,48}Te_3$ (p–typr`)	+ 175
3	tellurium	+ 300

In the presence of temperature gradient along conductor arises the flow of electrons from the hot end to the cold end. At the cold end accumulating negative charge, while at the hot – positive. This potential difference creates volume TEMF. In semiconductors, of electronic type electrical conductivity, this effect is stronger than in the metals, due to the fact that the concentration of electrons there increases with increasing temperature and accordingly the number of electrons passing from the hot to the cold end.

In p-type semiconductors at the cold end accumulated holes (positive charge) at the hot end- electrons, while in the electronic semiconductor- conversely. Therefore, in thermoelements consisting of hole and electron semiconductor TEMF arising in contact, sum of the TEMF branches that make up thermoelement.

At low temperatures, the accumulation of negative charge on the cold contact can further contribute to the fascination of electrons by phonons moving from the hot end (junction) to the cold.

In practice, often for the reliable operation of the equipment tend to increase the thermal conductivity of the insulating material without impairing its performance because the heat released by conductors, magnetic circuits and devices in general, to play in the environment through the insulation layer. Therefore, for increasing conductivity of typical dielectrics as polymers, they made in the form of compositions with inorganic filler. In Table 1.5. shown the values of the thermal conductivity of some materials.

Table 1.5. The values of thermal conductivity coefficients of some materials

№	Material	λ_T, W/(m*K)
1	Air	0,05
2	Bitumen	0,07

3	Paper	0,1
4	Genitacks	0,35
5	Fused quartz	1,25
6	Porcelain	1,6
7	Crystalline quartz	12
8	Graphite	18
9	Al_2O_3	30
10	Fe	68
11	BeO	218
12	Al	226
13	Cu	390

Thermal resistance – the ability of material withstand to rising temperatures and extreme changes in temperature (thermal shocks) without significant deterioration of performance properties. These properties can be mechanical or electrical resistance, optical properties, resistance to certain aggresive environments, etc. Thermal resistance is an important characteristic, as it affects the maximum allowable operating temperature of the apparatus as whole. To characterize the thermal stability of metallic materials operating at high temperatures, use the term heat resistance (resistance to deformation and fracture under the action of mechanical stress and high temperatures).

In the case of increasing temperature in materials can flow of possible different phenomena. Among them, it is advisable to select:

- melting of crystalline materials. Thus the material to become amorphous;
- softening of amorphous materials – causing strong reduction of mechanical strength, and in the presence of mechanical stress – their irreversible deformation;
- phase transitions in the solid state – change performance characteristics (typical for metal structural alloys, magnetic, ferroelectric, liquid-crystalline and other materials);
- burning, charring, oxidation or decomposition;
- changes in electrical characteristics;
- thermal aging of dielectrics – causes change in their structure and properties; it occurs as result of chemical processes under

prolonged exposure to elevated temperature and reduces mechanical and electrical parameters of the material. Thermal aging is amplified in the presence of oxygen, ozone when exposed to radiation, including visible and ultraviolet, electromagnetic fields and mechanical stresses. Heat aging are particularly exposed organic materials.

Thermal resistance of inorganic materials is significantly higher than the organic.

Cold resistance – the ability of material to maintain their properties at low temperatures. It is particularly important for organic electric insulating materials. At low temperatures, their electrical properties are improved, but they lose flexibility and elasticity, acquiring undesirable hardness and brittleness, which can lead to the destruction of materials.

In practice, often use the term operating temperature range indicates the lower and upper temperature limits to save all important performance properties.

Thermal conductivity- measure of the thermal inertia of the matter. This parameter characterizes the rate of temperature change of the material in the non-stationary thermal processes. Thermal conductivity coefficient (m^2/s) is determined by formula:

$$\alpha_T = \frac{\lambda_T}{\rho c} \qquad (1.52)$$

where ρ – density of the material; c – the specific heat.

§ 7. Mechanical properties

The mechanical properties characterized ability of material resisting to deformation (elastic and plastic) and destruction. Study of mechanical properties allows to obtain information about nature of material and behavior of impurities and defects that can be used for diagnostic purposes.

Mechanical properties include flexibility, strength of material (deformation resistance) and its plasticity (ability to change the shape and size without destruction).

Stress σ measured in pascals (Pa), deformation ε – in percentage (%) elongation $(\frac{\Delta l}{l}\cdot 100)$ or narrowing cross-sectional area $(\frac{\Delta S}{S}\cdot 100)$.

Strength is property of solids to resist irreversible change of form and destruction under the influence of external mechanical loads. The strength is determined by the interaction between atoms, ions, molecules, of which the material is formed.

Deformation – changing size and form of the body due to the change in the relative position of its particles. It takes place under the influence of external loads, and also under the action of internal stress fields occurring in the material structure. The main types of deformation: tension, compression, torsion, shear, bending. In the body (or in its parts) occur mechanical stress – normal σ and tangential (shear) τ. *Mechanical stress* – the amount of force (load) per unit cross-sectional area of the specimen.

To determine the strength characteristics of materials used schedules dependence of stress on the degree of deformation. Upon deformation changed not only geometrical parameters, also changed the structure and properties of material due to changes in the distance between the atoms. There are elastic and plastic deformation.

Elastic deformation – results from the displacement of atoms from their equilibrium positions in the crystal lattice over distance typically smaller period of lattice, and disappears after termination of the external force. In the field of elastic deformation is performed Hooke's law: $\sigma = E\varepsilon$, where E – modulus of elasticity, or Young's modulus. In the elastic region after removing the load length of sample and its cross section did not differ from the respective initial values, i.e. the material recovers its original shape and sizes. In practice, for assessing elastic limit measured apparent elastic limit- is the voltage corresponding to the occurrence of permanent deformation certain predetermined value (0,001; 0,003; 0,005%) In particular, for admission to the permanent deformation of 0.005% apparent elastic limit denote as $\sigma_{0,005}$.

Upon reaching the yield stress begins the process of *plastic deformation* of the material. Thus there is reduction in cross-sectional area of the sample. Plastic deformation is caused by the shift (slip) some parts of the crystal relative to the other, and does not disappear after removal of the load. The shift is effected by movement of dislocations in the crystal. The connection between the parts of the crystal is not disturbed, but changes the mutual arrangement of the atoms in the crystal lattice.

The magnitude of the load required for the plastic deformation is determined by the presence of dislocations and the possibility of movement.

For the deformation of an ideal crystal would need to make huge effort, as would require simultaneous shift of all atoms, so the theoretical tensile strength above the real about two orders of magnitude. Currently grown wire-like (whiskers) with very low dislocation density, the strength such crystals is close to the theoretically possible. The size of these crystals do not exceed few microns.

Monotonic relationship between the concentration of dislocations in material and its plasticity will occur only as long as the concentration of dislocations will not be so high that they begin to interfere to the movement relative to each other during the deformation of the material. The fact that the dislocation occurs around the deformed area that characterize excessive voltage. If the motion of dislocations has two areas of overlaping, for further dislocations shift relative to each other it is need to make much greater efforts. This manifests itself in the reduction of material ductility.

To the ability of material to plastic deformation strongly influences the type of chemical bonding. Materials with covalent and ionic bondings (C, Si, Ge, NaCl, glass, ceramics, etc.) under ordinary conditions is practically do not subject of plastic deformation, while many materials with metallic bonding, and some polymeric materials are very plastic.

In contrast to elastic deformation during plastic deformation break linear relationship between σ and ε. At some value of σ sample deforms without further increasing the load. Such phenomenon is called *flow* and characterized by yield strength (σ_T).

With further increase of σ increases the length of sample and occurs disruption. Disruption precedes formation of neck – drastic local reduction of its cross section. The strength of material is characterized by mechanical stress corresponding to the maximum load at which still no destruction of the sample. It is called the *tensile strength* or *ultimate resistance* ($\sigma_в$), it is conditional and is determined by the ratio of maximum load (F_{max})to the original sample area (S_0):

$$\sigma_в = \frac{F_{\max}}{S_0} \tag{1.53}$$

If then the load is removed, the sample is longer and thinner than before stretching, i.e. plastic deformation is irreversible. One of the characteristics of plasticity is the *elongation* of plastically deformed material:

$$\varepsilon = \frac{\Delta l}{l_0} \tag{1.54}$$

Another characteristic is the *relative narrowing* of plasticity:

$$\Psi = \frac{(S_0 - S)}{S_0} \tag{1.55}$$

For plastic materials these characteristics typically is ten percent.

Tensile strength is defined similarly tensile at compression:

$$\sigma_c = \frac{F_c}{S} \tag{1.56}$$

and at bending–

$$\sigma_b = \frac{1{,}5 F_b L}{(bh^2)} \tag{1.57}$$

where F_c, F_b –accordingly destructive force to compression and bending; L – distance between supports, under which arranged test sample; b, h – the width and height of the specimen.

At voltages greater than the tensile strength, deformation leads to *destruction of the material.* Moving dislocation encounter obstacles in its path (surface of sample, phase boundaries, grain boundaries, subgrain, etc.) which have high concentration and stress. In these places originate microcracks, which can then grow and spread throughout the sample.

The destruction can be viscous and fragile: at *viscous destruction* plastic deformation reaches high values and is necessary for the development of crack increasing effective stress. Viscous destruction characteristic of many metals and alloys, organic polymers, etc.

At *fragile destruction* plastic deformation is negligible, before breaking the neck is formed, for missing, cracks developed without increasing the load. The degree of *impact toughness* ($a_н$) of the material, which characterizes its strength of impact bending:

$$a_н = \frac{\Delta A}{S} \tag{1.58}$$

where ΔA – the work expended on the destruction of sample; S – cross-section area of sample.

The lower the value $a_н$, the more brittle material. In reality, the plastic deformation of material (the process of dislocation motion) occurs at greater voltages than the yield stress.

Hardening of the material may occur, for example, in the process of cold deformation. Plastic deformation from its inception to the moment of destruction is accompanied by increase in deformation resistance of the material as increase in its extent. This means that for the continuation of crystalline material deformation requires constant increasing of applied voltage. This phenomenon is called the deformation consolidation. This consolidation process continued by plastic deformation due to the continuous increase in the density of dislocations and is due to the motion of dislocations in different crystallographic slip systems, their mutual intersection, forming of "forest" dislocations, which complicates further plastic deformation of the crystal. Consolidation contribute also other defects that prevent the movement of dislocations: impurity atoms, its own point defects and their clusters (for example, dislocation loops, pores, etc.), allocation of second phases, grain boundaries and subgrain, interphase boundaries, etc.

Hardening of the material can be achieved not only by mechanical deformation (strain hardening) but also by heat treatment, doping, by irradiating it with high-energy particles (neutrons, ions, electrons), by laser irradiation.

An important operational and technological characteristics of many materials is the *hardness* – the resistance to local plastic deformation in the surface layer that occurring in the case introducing to it solid (indentor) material. Methods for determination of hardness is based on indentation to the material under constant load foreign body (ball, cone or pyramid) of certain sizes, made of material which hardness exceeds the hardness of the testing material. The hardness is determined by the relation of indentation strength:

- to square footprint that remains on the surface of sample (Brinell method, indicated as HB and number of hardness);
- to the depth of indentation (Rockwell method, indicated as HRB and number of hardness);
- to 1 mm^2 area of footprint (Vickers method, indicated as HV and number of hardness).

If you want to measure the hardness of small volumes, such as the amount of the individual grains, the method of determining the *microhardness* used, wmeasured at the diagonal indentation diamond pyramid with optical microscope. According to the hardness value can be judged on the strength and ductility of the material.

The increase in temperature is accompanied, as rule, with increasing the plasticity of materials and decreasing in their strength, elasticity and hardness. On this property based methods of heat treatment of materials by pressure (rolling, forging, stamping, drawing).

Other mechanical properties. With long-term effect of constant load the material can be subjected to further plastic deformation. This phenomenon is called *creep.* Especially strongly creep manifested at high temperatures. Resistivity of materials determines the strength of the material at high temperatures. Resistivity of materials determines the creep strength of the material at high temperatures (heat resistance). To evaluate the heat resistance of materials determine the *creep limit* – the maximum voltage at which the creep strain at given temperature for certain time reaches certain value. Note that creep could occur in the material under load even below the yield point.

To assess the material's resistance to deterioration by prolonged exposure to temperature and voltage determine the limit of long-term strength – the maximum stress, which under the influence of the material at given temperature is destroyed after specified period of time.

Long term effect on the cyclic material (alternating) load may lead to material *fatigue.* Fatigue is the process of gradual accumulation of damage in the material under the action of cyclic loads, leads to the changing in its properties, cracking and breakage. The main characteristic of fatigue is fatigue curve – the relationship between the amount of accumulated damage (deformation, micro- and macro-cracks) and the number of cycles or long-term presence of the material under cyclic loading. Fatigue cracks are generated in the structural imperfections of the crystal (often on the surface of specimen) and the number and rate of formation increasing with temperature. The property of material to resist fatigue called *endurance* and characterized by endurance limit – the maximum voltage that the material can withstand without failure for given number of loading cycles.

In the case of working details under frictional conditions occurs material deterioration- a gradual change in the size and shape of the body due to destruction of its surface. The amount of deterioration was determined by measuring the size or weight of the sample, sometimes by other methods. Properties of materials to resist deterioration is called *wear-resistance.*

Inorganic materials (glass, glass ceramics, ceramics) have greater hardness, lower ductility and substantially higher strength than organic. In most cases, they are prone to brittle fracture.

Organic material (high-molecular compounds) due to the peculiarities of the structure capable of under the influence of mechanical stresses develop significant reversible (highly elastic) deformation, reaching, for example, in rubber and gums hundred percent. However, their strength and toughness are relatively low. The general nature of the mechanical properties of organic materials are determined by the physical state of the initial polymers, the flexibility of the macromolecules, the presence or absence of the supramolecular structures, as well as the influence of specific additives (fillers, plasticizers, stabilizers, etc.) and external influences (temperature, electromagnetic fields, radiation, and other factors).

Technological properties. This properties characterize the ability of materials subjected to various treatments for producing goods and are often called the generalized notion of manufacturability. The main technological properties include:

Machinability. Good machinability involves obtaining smooth and clean surface of the material after treatment by cutter. Poor handling of the materials exposed to high viscosity, as well as hard and brittle.

Weldability, solderability – material's ability to form by means of welding and soldering stable compounds. When joining materials by these methods need to harmonize their temperature coefficient of linear expansion, the mutual wetting liquid.

Casting properties – the ability of material to form castings without cracks, voids and other defects. Good castability properties have materials with high fluidity (capable liquid fill without voids volume of the mold) and low shrinkage (volume reduction) when passing from liquid to solid. For metal alloys, besides important consideration segregation – inhomogeneous chemical composition over the volume of material that occurs during crystallization.

Workability pressure – the ability of material subjecte without destroying to pressing, forging, stamping, rolling, etc. at hot and cold state.

Chapter 2

CHEMICAL BONDINGS

§ 1. The structure of atoms and chemical bonding

Solids are ensembles of linked atoms between each other by certain way. Bondings takes place in the result of atoms (ions) interaction and the valence electrons, leading to decrease in potential energy of U_{pot} system, and above all, the energy of electrons involved in the bonding.

The equilibrium distance in solid between atoms (ions) – r_0 corresponds to the minimum of potential energy of the crystal lattice. r_0 is the distance at which attraction forces between opposite charges and repulsive forces between similar charges are balanced. With increasing distance more than r_0 strength of bonding decreases, and U_{pot} increases proportionately to $\frac{1}{r^n}$, where n depends on the type of chemical bonding and varies from $n = 2 \div 3$ (so-called *strong bonding* – covalent, ionic, metallic) up to $n = 6$ (*weak bonding* – Van-der-Waals). Type of bonding depends on the electronic structure of free atoms and, above all, from the structure of their valence shells.

Laws of the free atoms electronic structure are periodic table of D.I. Mendeleev. Electron state in isolated atom and the electron distribution of shells, subshells and orbitals determined by four quantum numbers.

Principal quantum number **n** determines the size of given electron shell in isolated atom, which is formed by electrons with the same principal quantum number. The electron energy is inversely proportional to n^2.

Orbital quantum number **l.** It defines the shape of the orbit and the magnitude of momentum of the electron motion and can take values from 0 to $(n-1)$. Electrons with the same quantum number $\boldsymbol{l}$ belong to the same subshell. Various subshell indicated by the following letters:

l	0	1	2	3	4	5
Designation of subshell	s	p	d	f	q	further on the latin alphabet

Magnetic quantum number m_e. It characterizes the plane orientation of the electron orbital in space. m_e can range from $-\boldsymbol{l}$ to $+\boldsymbol{l}$ (including 0) or $(2\boldsymbol{l}+1)$ values.

Spin quantum number m_s. It characterizes the orientation of electron intrinsic rotation relative to the axis *z*. m_s can take two values: $m_s = +\frac{1}{2}$ and $m_s = -\frac{1}{2}$.

The distribution of electron to orbitals subject to the Pauli exclusion principle and Hund's experimentally established rule. According to the Pauli principle, in atom can not be two electrons with the same four quantum numbers, i.e. on each orbit can be no more than two electrons with different spins (paired electrons). The maximum number of electrons in the *s, p, d, f* subshells respectively is equal to 2; 6; 10 and 14.

According to Hund's rule, this electronic configuration has the lowest energy at the maximum number of unpaired valence electrons. As an example, in Fig. 2.1. shown the distribution of valence 2*p*- electrons in isolated atom of carbon. They are placed one by one in two *p*-orbitals.

Filling of subshells occurs in the following sequence: *1s*, *2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s*, *4d, 5p, 6s, 4f*, *5d, 6p, 7s, 5f, 6d.* The energy of electrons in the filled orbit higher than filled. The nature and fullness of development of electron orbitals of the valence shell of atom determine the type of chemical bondings resulting in the formation of elemental substance. Elements are divided into metals (simple and transient), semiconductors and dielectrics (chemical bondings in dielectrics is not qualitatively different from bondings in semiconductors). Elements occupying the left and centeral part of expanded periodic table of elements – metals, and elements that occupy the right side – mainly semiconductors and dielectrics.

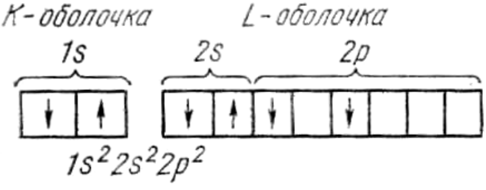


Figure 2.1. – The distribution of electrons in isolated atoms of carbon (ground state)

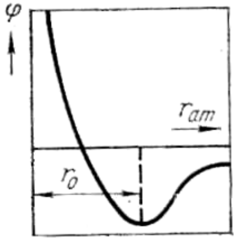


Figure 2.2. – Scheme of changing in the interaction potential between two atoms

Figure 2.2. – Scheme of changing in the interaction potential between two atoms $[\varphi = (r)]$ depends on the interatomic distances. In the beginning of coordinate placed fixed atom, r – the equilibrium interatomic distance, r – distance between atoms

In material science of semiconductors and dielectrics accepted subgroups placed in the left and central parts of the deployed periodic system (Table 2.1.): in which there are only metals, denoted by the letter *A*, and the subgroups, placed in the right side – by letter *B* (in chemistry usually accepted another notation: for *A*-subgroups (or for main subgroups) are those in which occur development of «*ns*-subshells at unfilled *(n–1) d*- subshells and construction of np-subshells, for *B*-subgroups (or secondary subgroups) are those in which occur building of *(n*−1) *d* и *(u–2) f* subshells and also *ns*-under-shells filled at *(n– 1) d*- subshells).

This table is taken from the book of Ch.Kittel "Introduction to the solid state physics": Trans. from English. – M .: Nauka. – 1978. Under the binding energy mean energy required for the separation of the solid body to individual neutral atoms at 0K.

Emphasize that the valence electrons can be not only external electrons, but also the previous shells. At approximation of isolated atoms and formation of ensemble of atomic electronic shells (primarily shells of valence electrons) overlap.

Table 2.1. Values of chemical bonding energy of number of elements, eV/ at

H 4,48																	He
Li 1,65	Be 3,33											B 5,81	C 7,36	N	O	F	Ne 0,02
Na 1,13	Mg 1,53											Al 3,34	Si 4,64	P	S 2,86	Cl	Ar 0,08
K 0,941	Ca 1,825	Sc 3,93	Ti 4,855	V 5,30	Cr 4,10	Mn 2,98	Fe 2,29	Co 4,387	Ni 4,435	Cu 3,50	Zn 1,35	Ga 2,78	Ge 3,87	As 3,0	Se 2,13	Br 1,22	Kr 0,116
Rb 0,858	Sr -	Y 4,387	Zr 6,316	Nb 7,47	Mo 6,81	Tc	Ru 6,615	Rh 5,752	Pd 3,936	Ag 2,96	Cd 1,16	In 2,6	Sn 3,12	Sb 2,7	Te 2,6		
Cs 0,827	Ba 1,86	La 4,491	Hf 6,35	Ta 8,089	W 8,66	Re 8,10	Os	Ir 6,93	Pt 5,852	Au 3,78	Hg 0,694	Tl 1,87	Pb 2,04	Bi 2,15			

The interaction of valence electrons belonging to different atoms, causes the splitting of electrons energy levels of discrete isolated atoms in the sublevels (the effect of "bump"). The energy within the nucleus is removed from appropriate level, the greater the distance between the approaching atoms from which starting splitting. Almost at the equilibrium interatomic distance r_0 (Fig. 2.2.) split levels of all electrons participating in the formation of bondings.

During occurring of chemical bondings change the wave functions of the valence electrons. The basic materials are three types of chemical bondings: metallic, covalent (homopolar) and Van-der-Waals. In the compounds and solutions can also ionic (heteropolar) bonding.

As rule, in complex, and often in elementary substances realizes mixed (heterodesmical) bonding. The main characteristics of the bonding are the binding energy, bond length, the energy spectrum of the valence electrons.

Under the *binding energy* understands the amount of energy that must be expended to break chemical bondings caused the formation of solid body, and translate its constituent atoms to free state. Quantitatively, the binding energy can be roughly estimated by the amount of energy that must be expended to move the valence electrons in the solid to free atom levels, or by sublimation heat.

The binding energy can be qualitatively characterize the bonding length, size of elastic modulus, melting temperature of material, material hardness (greater the binding energy, usually larger than the value of these characteristics).

Various chemical bondings give rise to different crystal chemical structures, each of which is characterized by its own, inherent spatial arrangement of atoms (ions) and consequently, its basis, the type of unit cell, coordination number and etc. The different chemical bondings are characterized by varying degrees of direction (various density distribution of the valence electrons in different crystallographic directions). Each crystal chemical structure is characterized by two lattice: crystal lattice and reciprocal lattice. The dimension of crystal lattice vector – the length (L), and dimension of the reciprocal lattice vector – inverse length (1/L).

The reciprocal lattice is constructed in the space of wave numbers κ. (There is one correspondence between the basic lattice vectors (a, b, c) and the main vectors of the reciprocal lattice $(a*, b*, c*)$: $a*a=2\pi$; $b*b=2\pi$; $c*c=2\pi$; $a*b=0$; $b*a=0$; $c*a=0$; $a*c=0$; $b*c=0$; $c*b=0$. It is noted that in crystallography (unlike physics and material science of solid) are generally in the above scalar product multiplier 2π is lowered and build reciprocal lattice in reverse space). The structure of reciprocal lattice as real as the structure of crystal lattice, and its importance is due to the fact that many wave processes in crystals, including the movement of valence electrons (as well as their distribution in energy), are largely determined by the structure of reciprocal lattice.

Consequently, crystal and reciprocal lattice defined by occurring chemical bondings in the case of combining atoms in the solid, therefore the detailed description of chemical bonding in one or another solid body can not be performed without analysis of its crystal and reciprocal lattices. In k-space is constructed zone whose surfaces correspond to the wave vectors of the electronic waves to be diffracted by the crystal lattice. This is the Brillouin zones.

For each crystal lattice in reciprocal space can be built set of Brillouin zone (first zone, second zone, n-zone). In Fig. 2.3 shown the first Brillouin zone for FCC lattice and diamond lattice. Brillouin zones are symmetrical polyhedra have symmetry elements of the point group.

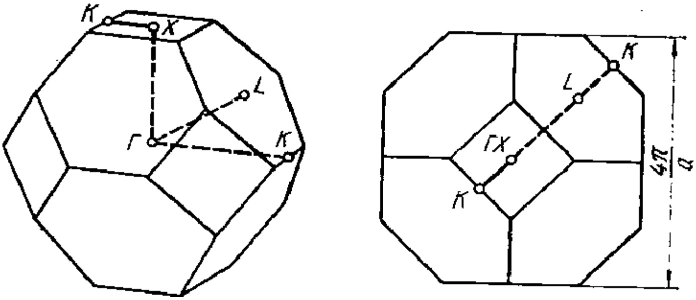


Figure 2.3. – Brillouin zones of FCC and diamond lattices

An important role in determining the band structure (more precisely, allowed and forbidden energy electrons zones) of specific substances play not only the surface but also symmetry elements of respective bands- Brillouin zone.

§ 2. The types of chemical bondings

Metallic bonding leads to the energy spectrum of valence electrons in solid when one of the zones arising from the electron levels of the free atoms, turns out of entire range of the existence of solid is only partially filled with electrons (more precisely, part of the states in the band is occupied). Metallic bonding results from the interaction of electrons and ionic core, wherein valence electrons delocalized in most cases, and belong to the lattice. In the simplest cases (for example, for simple metals in the IA subgroup) metallic crystal model as following: ion core immersed in the "electronic-liquid". The electron density distribution in geometrical space, there is usually no noticeable anisotropy. Bondings in simple A – metals are built easier than in transition metals and follows after by *d* and *f* filled subshells of metals and located in B – subgroups. The binding energy of simple A – metals usually considerably lower than for transition metals and *B*-metals arranged in the same period (see. Table 2.1.).

In addition, in common metals and non-metals bonding strength within one subgroup decreases with increasing number of periods, and usually in transition metals on the contrary increases.

Covalent bondings also result of valence electrons and ion core solid interaction. Covalent bonding carried out by pair of valence electrons with opposite spins, and in the case of pure substances, these electrons belonging to different atoms. During occurring covalent bonding orbit of valence electrons participating in the formation of bondings, overlap, thus, the greater the overlap, the stronger the bonding. For covalent bonding characteristic anisotropic distribution of density of the valence electrons. In the geometric space (covalent bonding – directional bonding). The valence electrons (more precisely, the electrons participating in the formation of bondings) are delocalized (do not belong to individual atoms), but staying them in different areas of the crystal lattice is different: the maximum probability (maximum density of valence electrons) observed in the direction of the shortest interatomic distances.

Covalent bondings are saturated in the sense that they can not occur covalent bondings with ordinary electron number greater than two.

Covalent bonding leads to the energy spectrum of valence electrons, when one of the zones that have arisen from the electron levels of free atoms, at 0 K is completely free (conduction band), while it is separated by energy gap (bandgap) of full-time band (the valence band).

Crystals, which are implemented ionic bondings consist of positively and negatively charged ions (Fig. 2.4.).

Ionic bonding is provided mainly by electrostatic attraction (Coulomb forces) that occur between oppositely charged ions. Ions finished its outer electron shell to stable configuration – nearest electron shell in the periodic system of inert gas – the addition of missing electrons (anions) or electron impact (cations). It should be emphasized, that complete separation of positive and negative charges, i.e. ideal ionic bonding, never carried out. Due to the wave properties of finding electron probability of valence electrons near the nucleus of the cation is small but never zero.

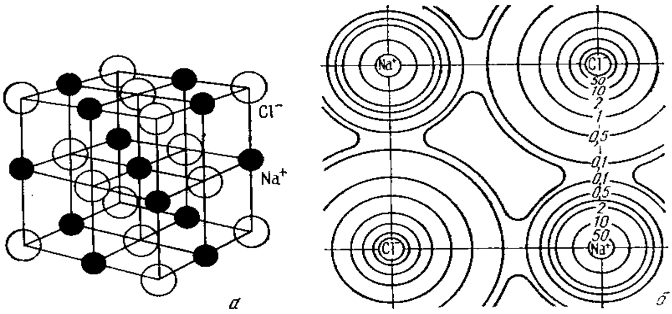


Figure 2.4. – Crystal structure of NaCl (a) and distribution scheme of electronic density in NaCl (b)

Therefore, in ionic crystals, along with electrostatic attraction of charged ions and coupling strength caused by the overlap of the electron orbits of valence electrons. The interatomic (interionic) distance in ionic crystals, and therefore their ionic radii, determined by equilibrium attraction forces between anions and cations and repulsive forces between their electron shells.

An important feature of ionic bonding – its polarizability due to the polarizability of ions. This is due to the fact that centers of the negative and positive ion charges do not coincide. The polarizability is characterized by dipole moment M, that proportional to the electric field strength and different product of charge Z_e to dipole distance d between the centers of ion positive and negative charges (Fig. 2.5.):

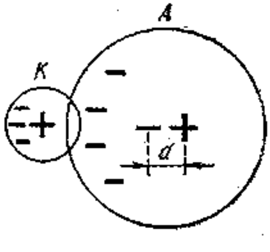


Figure 2.5. – Ion polarization scheme: K – cation (positively charged ion); A – anion (negatively charged ion)

$$M = \alpha * E = Zed,$$

where α * – proportionality coefficient called polarizability; E – electric field strength arising in the displacement of charges in ion.

The polarizability α is approximately constant for given ion. The larger ionic radius, the easier it is polarized. Therefore, anions generally are polarized more strongly than the cations. Below are values of α for some ions, located at 1A (Li^+, K^+) and VIB subgroups (O^{2-}, Se^{2-}, Te^{2-}), supporting this position:

ions	Li^+	K^+	O^{2-}	Se^{2-}	Te^{2-}
$\alpha*10^{24}$	0.0075	0.087	0.312	0.84	0.96
R, nm	0,068	0,133	0,146	0,192	0,221

These data show that within subgroup with increasing ionic radius polarizability increases.

Structure of ionic crystals, and hence the value of coordination numbers depend on the relative sizes of the anion and cation.

Stability conditions of the structure is that each ion contact with ions of opposite sign (Fig. 2.6). When ion contact simultaneously with ions of the same and opposite sign, the structure is less stable. Finally, if the size of smaller ion less than the size of ion (pores) between contacting large ions of opposite sign, obtained unstable structure and rearranged into one in which the above condition is satisfied (Fig. 2.6.).

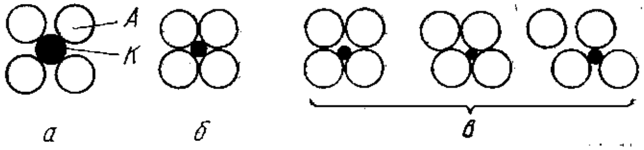


Figure 2.6. – Stability of ionic crystal structures depending on the relative sizes of anion (A) and cation (K). Stability of structures decreases in the direction of a → б → в

Therefore, for ionic crystals existed stability limits of structures with different coordination numbers. The values of these limits are determined by simple geometric relationships. Below are the limit values of ionic radii ratio, possible for structures with different coordination numbers:

Z_K	8	6	4	3
$\frac{R_1}{R_2}$	0,73 – 1,37	0,41 – 0,73 1,37 – 2,41	0,22 – 0,41 2,41 – 4,45	0,15 – 0,22 4,45 – 6,45

Energy of the crystal lattice in the case of ionic crystals is almost entirely determined by the Coulomb interaction (Coulomb energy or Madelung energy) and can be determined from the expression

$$E_p = \frac{-Ne^2\alpha Z_1 Z_2}{R_0} \tag{2.1}$$

where α – Madelung constant, taking into account the contribution to the energy of crystal lattice interaction of ions located near to the subject ion coordination spheres; *N* – number of ions per molecule equal to the number N_A, multiplied by the number of ions (∑m) in the molecule (see below). Z_1, Z_2 – valence of interacting ions; R_0 –the distance from considered ion to ions of the first coordination sphere.

Madelung constant in the theory of ionic bonding plays an important role. Consider its calculation on the example of NaCl. As ion with respect to which the calculation is carried out, choose sodium ion (its charge equal to + e). Sodium ion (see. Fig. 2.4, *a)* is surrounded by six negative chloride ions (first coordination sphere), located at distance R, twelve positive sodium ions (second coordination sphere) at distance $R\sqrt{2}$, eight negative chloride ions (third coordination sphere) on distance $R\sqrt{3}$, six positive sodium ions (fourth coordination sphere) at distance of $R\sqrt{4}$; twenty-four negative chloride ions (fifth coordination sphere), located at distance $R\sqrt{5}$ and etc. Clearly, that placement of the ion coordination sphere depends on the type of lattice. A similar calculation would be obtained, if the ion relative to which provided calculations and would be selected chloride ion Cl^-.

The binding energy of one ion in the lattice of NaCl, taking into account the Coulomb interaction is:

$$-\frac{e^2}{R}\left(\frac{6}{\sqrt{1}}-\frac{12}{\sqrt{2}}+\frac{8}{\sqrt{3}}-\frac{6}{\sqrt{4}}+\frac{24}{\sqrt{5}}+\dots\right).$$

The alternating series in brackets is the Madelung constant α for NaCl. Essentially Madelung constant takes into account the development of coordination spheres and the distance between the coordination spheres. The value of series number constituting the Madelung constant, determined by the structure of crystal lattice, and the sum of the series has certain value. Below are the values of Madelung constant α and the value of Σm for series of crystal structures:

Crystal structures	α	Σm
Sodium chloride (NaCl)	1,747565	2
Corundum (Al_2O_3)	4,17	5
Cesium chloride (CsCl)	1,762675	2
Zinc blende (ZnS)	1,6381	2

In Table 2.2. shown calculated and experimental values of the crystal lattice energies (binding energy) for some ionic crystals.

Table 2.2. The values of the binding energies of alkali-halide crystals with structure of sodium chloride

crystal	(R_A+R_K), nm	Binding energy, kJ/mol	
		experiment	calculation
LiK	2,014	– 1015,2	– 1014,8
LiCl	2,570	– 833,4	– 808,3
LiBr	2,751	– 793,3	– 758,4
LiI	3,0	– 744,6	– 696,0
Note. All values for room temperature			

Polarization bonding (or van-der-Waals forces type bonding) observed in molecular crystals, as well as some semiconductors and dielectrics crystals (along with other types of bonding). Molecular crystals include crystals of rare gases like Ne, Ar, Kr, Xe, and also crystals of I_2, Cl_2, O_2, HCl, HBr, H_2O, CO, NH_3 and other substances. Most molecular crystals (e.g., in I_2, Cl_2, O_2, HCl etc.) distinguished two types of bondings: intramolecular and intermolecular. Intermolecular bondings, and the bondings between inert gas atoms in crystals and are bondings of the Van-der-Waals forces. Typically, these bondings are much weaker than intramolecular, but they define number of important properties, in particular melting temperature of the molecular crystal. The basis of the -der-Waals type of bonding is the polarization of the molecules forming the molecular crystal.

Below are some of the properties of molecular crystals, calculated according to formula (2.2):

crystals	Ne	Ar
H_{subl}, kJ/mol	2,47	8,51
E_p, kJ/mol	1,97	8,72
T_m, K	24	84

Polarization and dipole moment in this case arises due to the fact that the thermal fluctuations of atoms forming the molecule, the centers of gravity of the positive charges (nuclei) and negative charges (electrons) having different mass and therefore the inertia, are displaced relative to each other.

In Figure 2.7. schematically shown the main types of chemical bondings in solid crystals.

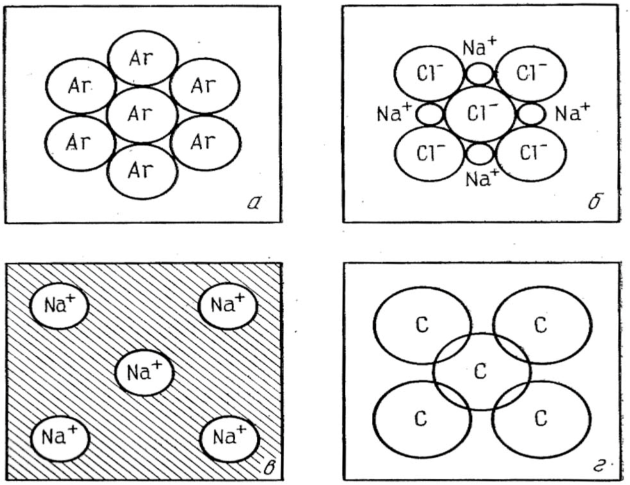


Figure 2.7. – Main types of bonding in crystals: *а* – van-der-Waals; *б* – ionic; *в* – metallic; *г* – covalent

The energy of crystal lattice with van-der-Waals bonding is calculated by the following formula:

$$E_p = U_{0T} + U_1 + U_2 + U_3 \qquad (2.2)$$

where U_{0T} − repulsion energy of molecules [$U_{0T} = -b \exp(-R_o/\rho)$, where R_o − the distance between the centers of molecules, b and ρ – constants determined empirically]; U_1, U_2, U_3 − attraction energies related with the dipole interaction of molecules; U_1 − orientational interaction energy of caused by its own electric dipole moment of the molecule ($U_1 = -\frac{A}{R_0^6}$, where A depends on the magnitude of dipole moment and temperature); U_2 –energy of the induction interaction induced by dipole moments of molecules, induced under the influence of surrounding molecules ($U_2 = -\frac{B}{R_0^6}$, where B depends on the value of induced dipole moment, temperature and polarizability of molecules); U_3 –energy of dispersive interactions caused by fluctuation of the dipole moment in molecules in the molecular crystal, due to accidental mismatch of electron " gravity centers " and nuclear charge ($U_3 = \frac{C}{R_0^6}$, where C is dependent of temperature, molecular polarizability and intrinsic frequency of molecules vibrations) .

§ 3. Chemical bonding and atomic and ionic radii

An important characteristic of chemical bonding is the length equal to the shortest interatomic distance in solids. In elements arranged in the same subgroup of the periodic system and forming substances with one type of chemical bonding, with increasing atomic number increase shortest interatomic distances (increasing the length of single chemical bondings) and decreases the strength of chemical bondings (exception is transition metals). The values of the shortest interatomic distances in condensed matter are described by the atomic and ionic radii. Under *atomic radius* of the element is generally understood half of the shortest equilibrium interatomic distances in the crystal lattice of element. The value of the atomic radius of chemical element remain approximately constant in all phases, which is involved in the formation of this element, if the type of chemical bonding, and coordination number in these phases are same as in chemical element. However, if type of chemical bonding changes, or during saving of bonding type varies the coordination number, the atomic radius of element takes new value.

Thus, each chemical element can be characterized by the set of atomic radii that describe the size of its atoms in the formation of metallic, covalent and van-der-waals bondings. Often use the term "metal element atomic radius for coordination number equal ...", "covalent atomic radius of element coordination number equal to ...." For example, tetrahedral covalent radius of element describes the size of its atoms in phases with covalent chemical bonding and with coordination number equal to 4, and octahedral covalent radius of the same element describes the size of its atoms in phases with covalent bondings, but with coordination number of 6.

Influence of the type of chemical bonding on the atomic radii of the magnitude seen from the following examples. In the crystal structure of semiconductor elements of VB subgroup exists two types of bondings: covalent and Van-der-Waals. The distances between atoms linked by covalent bonding, significantly less than the distance between neighboring atoms bonded by the type of van-der-Waals forces (for arsenic, these distances are 0.251 and 0.35 nm, respectively). A similar phenomenon is observed in metals. For example, zinc crystallizes in hexagonal lattice with the ratio c/a=1,86, the distance between neighboring atoms in planes {0001} is equal to 0.26649 nm and between neighboring atoms in adjacent planes {0001} is equal to 0.29129 nm. In such cases, the atomic diameter can be selected in different ways: as minimum distance (and this is preferred) or as an arithmetic mean.

The atomic radius dramatically changes with the coordination number. Increasing in the coordination number is always accompanied by increase in the atomic radii. The relative difference in the values of atomic radii corresponding to two data of coordination numbers in the structures of the same type of chemical bonding is kept roughly constant. Below are the conversion coefficients ($R_{Z_k}/R_{Z_{k=12}}$) for the values of the atomic radii (R_z) in structures with different coordination numbers ($Z_к$):

$Z_к$	12	8	6	4	3	1
$\frac{R_{Z_K}}{R_{Z_K=12}}$	1,0	0,97	0,96	0,88	0,81	0,72

The atomic radii of the elements can be compared only with the same coordination number and the same type of chemical bonding. For example, if we consider the atomic radius of aluminum in the substitutional solid solution and silicon (solid solution crystallizes to the cubic lattice of diamond Z_K=4), the atomic radius of elemental aluminum (crystallizes to the FCC structure with Z_K=12) should be given the value of tetrahedral covalent radius with Z_K =4.

When the polymorphic transformations of solids occur change of the crystal structures, accompanied by change in the atomic radii. For example, at 906 °C, iron from the γ-modification (FCC lattice, compact ratio η^*=0,74, Z_k=12 passes while cooling in α-modification (BCC lattice η =0,68, Z_k = 8), wherein the atomic radius of metallic iron reduced to 3%, and the specific volume of iron (ΔV_{sp}) increases to 0.8%. If during the transition to γ-Fe, α-Fe atomic radii remained unchanged, specific volume increase to huge size: V_{sp}= 9%. (Here η * – the ratio of the volume occupied by atoms in the unit cell to the cell volume: $\eta = V_{at} / V_{cell}$).

It should be noted that the value of atomic radius of the element depends on the temperature, pressure, composition of phase (particularly in solid solutions is observed deviation from Vegard's rule), but the effect of these parameters on the value of atomic radius is small and this allows extensive use of idea about atomic radii at considering the crystal-chemical structures of different phases. The atomic radius is usually measured in nanometers with accuracy of four sign after comma and precisely – to the seventh.

In crystals of elemental metals with FCC, BCC and г. к. lattices (with the ratio c/a=1,633) atomic radius is defined as half of the interatomic distance between the nearest atoms. In the case of solid solutions metal atomic radii are changed in complicated manner.

In crystals of elementary semiconductors by covalent radii understand half of the interatomic distance between the nearest atoms connected by single covalent bonding: covalent radii peculiarity is their approximate constancy in different covalent structures with the same Zк. Thus, the distance in single C—C bonds in the diamond and saturated hydrocarbons substantially identical and equal to 0.154 nm. It allows to estimate the unknown covalent radii of elements as follows. Let A element (covalent radius is unknown) forms AB compound with covalent bondings, in which R_{kovB} known. Then the covalent radius of element A is equal to: $R_{kovA} = R_{A-B} - R_{kovB}$.

The ionic radii may not be defined as the sum of half the distance between adjacent ions. Typically, the size of cations and anions differ dramatically. Moreover, the symmetry of ions is different from spherical. There are several approaches to estimating the values of ionic radii. Based on these approaches evaluate the ionic radii of the elements in compounds, and then found out experimentally determine interatomic distances ionic radii of other elements. Direct experimental method allow to get picture of the electron density distribution in the crystal, and thus of the true ionic radius is X-ray diffraction method.

§ 4. Features of chemical bondings in metals and semiconductors

Solids having metallic properties, or metals, can be seen as set consisting of two subsystems: the vibrating ions subsystem forming in space periodical structure, and subsystems relatively free of extended and itinerant electrons. In the result of the interaction of electrons with itinerant subsystem of ions of allowed and forbidden energy electrons. The main difference metal from other solids is that in metal the valence band are occupied by electrons only partially. Therefore, the conductivity of metal is associated with the movement of electrons in the valence band, and concentration of charge carriers is weakly dependent on the temperature and the order of magnitude in most cases is equal to 10^{22} cm^{-3}.

Metallic bondings are undirected and unsaturated character. Experimentally non-direction of bondings supported by the fact that the electron density of the valence electrons is almost evenly distributed over the volume of many metal crystals, and unsaturation – the ability to form solid solutions with high concentration of elements of different valence. The valence electrons interact with ions compensate the repulsive forces between ions (free electron model).

Energy collectivized valence electrons in metals is quantized. Therefore, the valence electrons in the allowed energies bands can have only discrete values of energy, but the difference between adjacent energy levels is very small ($\sim 10^{-22}$ eV).

In metals, the valence electrons tend to occupy the lowest energy levels.

The valence electrons are moving in positive ions lattice of that create the potential periodic field (the periodic potential), which period coincides with the interatomic distances.

The presence of forbidden energy bands due to the wave nature of electrons.

Metals, depending on the structure of the valence shell of free atoms are divided into simple and transient.

Ordinary metal of d-and f-subshell either empty or fully built up. In transition metals occur construction of *(n*–1)d- *and* (*n–2)f*-subshells, usually in the presence nS-electrons base metals are arranged in the of IA, IB, IIA, IIB, IIIB – IVB subgroups and transition metals – in IIIA – VIIIA subgroups of the periodic system. All alkali metals (subgroup IA) have BCC lattice, and their first Brillouin zone is rhombic dodecahedron. The electron concentration in them is 1 electron/atom and, therefore, the Brillouin zone is only partially filled, and Fermi surface is sphere. In Table 2.3 shown some properties of the alkali metals and metals of IB subgroup. Visible correlation between the position of the metal in periodic table and its properties. With increasing atomic number, atomic radius and lattice constant increases, decreasing the binding energy (and therefore the melting temperature), Fermi energy, increases mobility, decreases m^*.

Also have interest comparison of the structure of alkali metals and metals of IB subgroup- copper, silver and gold, having the same valence shell ns. These metals, unlike alkali crystallize to the FCC lattice.

Their first Brillouin zone is cuboctahedron, and these substances are good conductors.

Cuboctahedron is less symmetrical figure than rhombic dodecahedron. The Fermi surface of these materials deformed Brillouin zone: the Fermi surface "sticks" to the {111} faces of the Brillouin zone. This leads to the fact that the Fermi surface from closed (similar to that implemented in IA subgroup metals) goes out to the open.

Table 2.3. Some properties of metals in group I

Metal	**Z**	E_b^{*1} (calculation), эВ	a, nm	T_m, K	m^* near $E_Ф$	σ, Sm/sm, at 293K	μ, $sm^2/(V*s)$ at 293K	χ, J/(s*m*K) at 293K
IA subgroup								
Lithium	3	1,9	3,5	459	1,33	$8,6*10^6$ *2	18	-
Sodium	11	1,3	4,28	371	0,965	$2,1*10^6$	53	134,1
Potassium	19	0,85	4,34	340	0,86	$6,2*10^6$ *2	-	-
Rubidium	37	0,74	5,62	312	0,78	$11*10^6$ *2	-	-
Cesium	55	0,63	6,08	303	0,73	$19*10^6$ *2	-	251,4
IB subgroup								
Copper	29	2,8	3,608	1356	1,0	$5,82*10^6$	32	385,5
Silver	47	2,2	4,078	1233	1,0	$6,15*10^6$	56	423,2
Gold	79	2,22	4,070	1330	0,994	$4,09*10^6$	30	297,5

*1 – $E_b = \frac{2}{5} E_Ф$; *2 – At 273 K

In Fig. 2.8 shown the construction of the first Brillouin zone and Fermi surface of copper, gold, silver. Thus, the Fermi surface of these substances forms system of spheres connected by an isthmus in the <111> direction (Fig. 2.8). The latter is caused by the fact that the (n-1)d-subshells have entirely filled valence s- and p – bands strongly overlap and the density states of Eph is high. Especially copper, silver and gold is also very small compressibility compared with compressibility of alkali metals. This is due to the fact that they are filled with (n–1)d- subshells are relatively large, and filled subshell do not compress well.

Copper is widely used for electrical purposes, and its alloys – brass and bronze – as construction materials. Gold and its alloys, including Au-Ag alloys is used as contact materials in semiconductor devices. Copper and silver are the main components of semiconductor A^IB^{VII} compounds. In IIA and IIB subgroup situated simple metals like: beryllium, magnesium, calcium and strontium (IIA); zinc, mercury and cadmium (IIB).

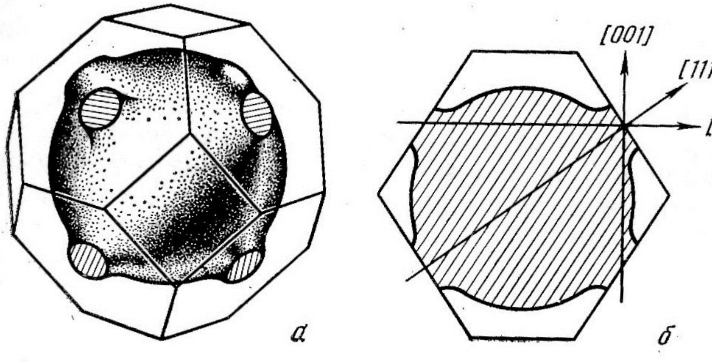


Figure 2.8. – Fermi surface of copper, silver and gold (a) and its section (b)

A feature of this group of metals is that most of them have г. к. lattice. Fermi surface of IIA subgroup metals are not spherical. It distorted by the top of Brillouin zone.

Metals of this group characterized by the overlap of *s* and *p*- bands, and sufficiently high density of states near the Fermi level, providing good metallic properties. The exception is beryllium, which the density states near the Fermi level is low. This explains the presence number of anomalies in the beryllium makes it atypical metal: low heat capacity, anomalous magnetic properties and others. The anomalies of beryllium include is axial ratio c/a: it is equal to 1,568.

Group II elements play an important role in the semiconductor electronics. Cadmium and mercury are included as major components in $A^{II}B^{VI}$ semiconductor compound and magnesium – more complex compounds. Some elements of Group II are used as doping acceptor impurity in $A^{III}B^{V}$ compounds.

From metals with fully completed *d* and *f* –subshell remains under consideration III metals (aluminum, gallium, indium and thallium) and IV (tin, lead) groups.

Aluminum is the most important material of contacts and interbondings (systems of metallization) in semiconductor devices and integrated circuits, is included as A^{III} main component to many $A^{III}B^{V}$ compounds solid solutions on their basis as well as in the commonly used dielectric substrate material of sapphire (α-Al_2O_3). Great importance have its use as the basis of light alloys commonly used in the aviation industry and in construction.

Gallium and indium are used as the main components of the most important semiconductor $A^{III}B^{V}$ compounds. Elements of III group are acceptor additives in elementary semiconductors -germanium and silicon.

Lead is a major component in the semiconducting compounds of $A^{IV}B^{VI}$ class, in the composition of contact alloys and solders in semiconductor devices based on germanium, $A_2^{V}B_3^{VI}$ thermoelectric class of compounds, and others. Metal properties has β-tin ("white tin") – high-temperature modification of tin, β-tin has tetragonal lattice, and low-temperature modification of tin – α-tin ("gray tin") has diamond like lattice with covalent bondings and it is a semiconductor. Lead is more metallic than tin, and has FCC lattice.

The transition metals take average place of the 4, 5, 6, and 7th periods (subgroup IIIA – VIIIA).Their amount in the 4th, 5th and 6th periods (except for lanthanides and actinides) is 24. A feature of these elements is that they are internal completion (n-1)d- and (n-2)f-subshells.

It is assumed that due to the transition metals are involved not only the s-, also d- electrons.

Not all of transition metals having uncompensated valence electrons in atomic orbitals and have ferromagnetic properties. For the presence of ferromagnetic properties has yet to comply with the conditions of favorable exchange interaction between s- and d-electrons of neighboring atoms. It is observed when $\frac{2r}{d_{el}} = 2 \div 5$,, where 2r – the distance between the nearest atoms in the lattice; d_{el} – the diameter of the electron orbital with uncompensated spins. This requirement is met by iron, cobalt and nickel.

If $\frac{2r}{d_{el}} \rangle 5$ exchange interaction decreases sharply, and metal is paramagnetic, such as titanium. If $\frac{2r}{d_{el}} \langle 2$ strong exchange interaction leads to antiferromagnetism as, for example, in manganese.

Hybrid orbitals apparently responsible for the presence of certain transition metals covalent component of chemical bonding. An indirect confirmation of this data can serve as the sign of the resistivity changes at melting of iron, nickel and copper. While in the simple metals (aluminum, nickel, and copper) ρ increases during melting, in most transition metals (iron, manganese, etc.) this value is reduced. This means that during melting of nickel and copper probably enhanced scattering of conduction electrons, and does not change the type of bonding whereas during melting of transition metals, possibly reinforced metal component of bonding.

Participation in bonding not only ns, but also (n-1)d- and (n-2)f-electrons is responsible for high strength of the interatomic bondings in the transition metals, increases with increasing number of the period; in simple metals – on the contrary. Among these metals existed most refractory metals: chromium in the fourth period (t_m=1850°C), in the fifth – molybdenum (t_m=2625°C), in the sixth – tungsten (t_m=3650°C). The most refractory metals are located approximately in the middle of each period.

The complex nature of the electronic structure responsible, apparently, very common phenomenon among the transition metals of polymorphism, the cause of which is the change in the electronic structure with increasing temperature.

Participation in the electronic bondings of several orbitals (s, d, f) is explained, apparently, different valence transition metals in interaction with other elements. Proof of this is the fact that the transition metals form with elements of IV group large number of compounds. Thus in the reaction with the silicon tungsten forms three compound (silicide); titanium, chromium and other metals – five; vanadium, tantalum, iron – six; zirconium – seven; nickel – eight; manganese – eleven.

In each of double systems silicon – a transition metal with the increase in the compound proportion of the transition metal increases the metal proportion of bonding and its contribution to the properties.

Silicides are attracting increasing attention as material for interconnection (metallization) in integrated circuits.

Some transition metals are superconductors. *Superconductor* called a substance, which, starting from certain (critical) temperature T_c, the resistivity falls to zero. T_c of some transition metals:

metal	Nb	Tc	V	Ti
T_c, K	9,5	8,0	5,3	0,4

On the basis of iron obtained major structural, magnetic, stainless and other alloys. Nickel is also used in electro-vacuum technique as cathodic material. Titanium-based alloys exhibit the highest specific strength of all structural alloys. In combination with high corrosion resistance this making titanium-based alloys excellent structural material used in various technical fields, including in aircraft. Tungsten, molybdenum, niobium, tantalum and other refractory metals are widely used as heat-proof and heat-resistant metals, including in electro-vacuum technique. Some transition metals are used as dopants in semiconductor materials.

The founder of semiconductor materials science is academician A.F. Ioffe, who emphasized the role of short-range order in the structure and its influence on the properties of semiconductors: "...The primary characteristic of semiconductor can be considered structure of the electron cloud within the cell. Because of the nature of valence bondings in the cell flow physical and chemical properties of the semiconductor. "

It is experimentally shown that in crystals with covalent bonding, the electron density of the valence electrons substantially evenly distributed in space. In the shortest directions of two neighboring atoms, the electron density (the probability of electron) is higher than in other directions. This means that valence electrons which are localized in space and form "electronic bridges". Bonding has pronounced directional character, which is the most important feature of covalent bonding, in this case valence electrons are continuously moved along the bondings within the entire crystal.

Carried out bondings with pair of valence electrons in the total for two neighboring atoms linking orbit. In the case of elementary substances, each of the pairs of atoms, "gives" to bonding one valence electron. Thus, to form covalent bonding necessary of being two unpaired electrons of opposite spin orientations. In the formation of covalent bonding each atom efficiently completes its valence shell to 8 electrons by bonding electrons nearest neighboring atoms in the lattice.

Hume-Rothery first show that the structure of covalent crystals of chemical elements belonging to different groups of the periodic system and satisfies the rule:

$$Z_K=8-N \tag{2.3}$$

where Z_K – coordination number; N-number of the group which arranged element (N adequately valence of element). Z_K is the number of covalent bondings of atom.

Covalent crystal structure determined by the Hume-Rothery rule and direction of bondings, which can be found from the analysis of wave functions of the valence electrons. The strength of chemical bondings depends on the degree of overlaping of orbital with valence electrons: the greater the overlap, the stronger the bonding. Overlap of hybrid orbitals of neighboring atoms in the direction of shortest distance between atoms is more than possible overlapping of non-hybrid orbitals.

The development of performances series, allowing to determine the direction of chemical bondings in crystal. These ideas form the content of the theory of directed valences. The basis of this theory is based on two principles.

1. Covalent single (or simple) bonding is formed by the interaction of two electrons with opposite spins belonging to different atoms.
2. The direction of covalent bonding must comply with the direction in which the orbit of valence electron in the maximum degree overlaps by orbital of other paired valence electrons belonging to another atom.

Covalent bonding carried by one electron pair (single or simple bonding) is called σ – bonding. There may be occasions when two atoms are connected by multiple covalent bondings (in bondings involved more than two electrons). There are multiple π – and δ – bondings. Thus, covalent bondings, in contrast to metal characterized by orientation and saturation.

Covalent bonding give rise to specific crystalline structures, as well as the originality of the energy spectrum of valence electrons. The main feature of this identity – the presence of the bandgap energies between the valence band and the conduction band, and bandgap (E_g) dependent on temperature and pressure. In semiconductor at 0 K, the valence band is completely filled and the conduction band is empty, therefore, the electrical resistance of semiconductor at 0 K tends to infinity. Increasing of temperature from 0 K gives rise to lattice temperature fluctuations, ensuring the transfer of electrons from the valence band to the conduction band. Thus, if $T > 0$ K in the semiconductor, electrons emerge in the conduction band and holes in the valence band. The carrier concentration in bands, especially at low temperatures is small.

In intrinsic semiconductor, the Fermi level can be regarded generally as the level, which is excitation of electrons and holes when casting them as result of temperature fluctuations in the conduction band and valence band. The position of the Fermi level in intrinsic semiconductor differs sharply from the level position (surface) of Fermi in the metal; in addition, the concept level (surface) of Fermi for metal and semiconductor includes different physical content.

Elements of IV B subgroup – carbon (diamond), silicon, germanium, α - tin. Valence shells of free atoms of these elements consist of $(ns)^2(np)^2$ –electrons. sp^3 bonding- hybrid tetrahedral angle with $109^0 28'$.

Hybrid binder of orbitals formed by the interaction of the valence electrons, the wave functions of which are: Ψ_{3s}– Ψ_{3p} for silicon, Ψ_{4s}– Ψ_{4p} for germanium and Ψ_{5s}– Ψ_{5p} for α – tin. All these functions are similar to Ψ_{2s}– Ψ_{2p} for diamond.

The above mentioned elements of IVB subgroups have diamond-type lattice, which can be represented as formed by two FCC lattice inserted into one another and mutually displaced along the space diagonal to one-quarter of its length.

To one cell of lattice have eight atoms with coordinates (000, 0 $\frac{1}{2},\frac{1}{2};\ \frac{1}{2}\ 0\ \frac{1}{2};\ \frac{1}{2}\ \frac{1}{2}\ 0;\ \frac{1}{4}\frac{1}{4}\frac{1}{4};\ \frac{1}{4}\frac{3}{4}\frac{3}{4};\ \frac{3}{4}\frac{1}{4}\frac{3}{4};\ \frac{3}{4}\frac{3}{4}\frac{1}{4}$). The arrangement of atoms such that each of them is surrounded by four equidistant neighboring atoms (the coordination number is 4), forming tetrahedral group. Covalent bondings are directed along the <111> and continuous permeate "bonding" of entire crystal. Elements of diamond symmetry – $3L_4$. $4L_3$. $6L_2$. 9p, C. The coordinates of the center of symmetry $\left[\frac{1}{8},\frac{1}{8},\frac{7}{8}\right]$.

Compact factor of lattice-type diamond is 0.34, that is, half less than for BCC. Internode are tetrahedral and octahedral voids. The radius of the sphere inscribed in the tetrahedral and octahedral interstices, close to the radius of atom.

Such looseness of lattice due to the bonding direction, which significantly affects to the features of point defects formation (lighter than in metals forming Frenkel defects), the solubility and diffusion of impurities in the diamond-like semiconductors.

The energy spectra of valence electrons in crystals of IVB subgroups elements is different, and the structure of valence bands of these substances are less dependent on the individual characteristics of the chemical bonding than structure of the conduction bands.

Consider the results of study of the silicon and germanium band structure. Since the translational symmetry of diamond lattice is the same as for FCC lattice, the first Brillouin zone of substances with the diamond structure is cuboctahedron.

The shape of Brillouin zones depends only on the lattice structure. Therefore Brillouin zone substances having different chemical bondings, but which crystallize in similar structures are similar.

In the formation of crystals of germanium and silicon valence s- and p- levels of free atoms are split into two groups, creating two non-overlapping zones of allowed energies – the valence band and the conduction band. Extreme points of the conduction band of germanium and silicon lie on the axis of symmetry of the first Brillouin zone (the axis of symmetry of the first Brillouin zone in k-space: the direction of <111> and <100>, total 14 axes of symmetry: 8 <111> and 6 <100>).

The structure of the conduction band of silicon and germanium is different. In silicon minimums of conduction band are associated with at least minimum of one p- bands, which located in <100> near the X points. Because of the symmetry conduction band has such six minimums (valleys). The surfaces equal to electron energy (isoenergetic surfaces) are spheroids. In the conduction band of silicon s-band lies above p – band.

In the conduction band of germanium mutual arrangement of s- and p-bands is different: minimums of the conduction associated with minimums of s-bands and located in <111> at the boundaries of the Brillouin zone; totally existed such eight minimums (valleys). Isoenergetic surfaces are semi-ellipsoids of rotation. Thus, silicon and germanium are multivalley semiconductors with an energy equivalent to valleys. The dependence of electron energy on the quasimomentum near the minimums in silicon and germanium described by parabolic anisotropic dispersion laws. At thermodynamic equilibrium the conduction electrons are evenly distributed between the valleys. Due to the fact that the ellipsoidal surfaces of equal energy in conduction bands of silicon and germanium are arranged symmetrically, some electrical properties (electron mobility etc.) are isotropic.

Equivalence of "valleys" in the conduction bands in germanium and silicon may be broken during the deformation (for example, uniaxial compression) of the crystal, in this case the energy of electrons in one valley may increased, while in others –

decrease. This in turn can lead to redistribution of the electrons between the valleys and, consequently, to change the resulting properties (for example, changes in electron mobility and hence change in electrical conductivity).

The valence bands of silicon and germanium are similar: they consist of three energy bands. Two of these bands meet in the center of the Brillouin zone, the third cleaved from the first two by small band of the spin-orbit interaction. Thus, the maximum of the top of valence band in silicon and germanium located in the center of the Brillouin zone. The density of states in the valence band of germanium and silicon is four electrons per atom. Laws of holes dispersion in the valence band are not parabolically isotropic and distinguished from dispersion law of electrons in the conduction band. It should be emphasized that in the case of non-parabolic isotropic dispersion laws of electrons and holes (i.e. those areas dispersion characterized germanium and silicon) effective mass of the states density of electrons and holes (m_{nd} and m_{pd}) and effective masses of electrons and holes that define the mobility ($m_{n\sigma}$ and $m_{p\sigma}$) did not equal. The resulting value of the effective mass in the case of several types carriers, determining the carrier mobility in electric field called as *effective mass of conductivity.*

According to the band structure diamond is similar to silicon. Common in the band structure of diamond, silicon and germanium crystals is the fact that at minimum of conduction band bottom does not coincide with the maximum of valence band, and therefore in these substances can only be indirect transitions.

Tin has polymorphic transformation. Low-temperature semiconductor modification (α-Sn) with diamond structure transform to high temperature metal modification (β-Sn) with the structure of tetragonal lattice. Said polymorphic transformation due to the rearrangement of covalent tetrahedral bondings to metallic. Changing of bonding type in the transition α-Sn → β-Sn is the reason that it is accompanied by very sharp decrease in volume (more than 20%). This polymorphic transformation demonstrates common situation that number of substances and compounds may be either in semiconductor or in metallic state, depending on temperature and other parameters related to external influences. Therefore, it would be better to talk about the metallic and semiconducting (insulating) state of matter.

The band structure of substances regularly varies depending on their position in the periodic table of elements.

In Table 2.4. shown data of some properties of these elements. With increasing atomic number bondings regularly attenuated, reduced bandgap and increasing the proportion of metal component bonding. In lead following after tin chemical bonding loses direction and becomes metallic.

Table 2.4. Some properties of elementary semiconductors arranged in IVB subgroup

Substance	Number in periodic system	a, nm	E_b, eV/at	T_m, K	E_g, eV, at temperature, K		μ_e, at 293 K, $sm^2/(V*s)$
					0	300	
Diamond	6	0,35661	7,36	3700^*	-	5,2	~ 1800
Silicon	14	0,54282	4,64	1688	1,21	1,1	~ 1550
Germanium	32	0,5657	3,87	1210	0,78	0,67	~ 4400
α- tin	50	0,64912	3,12	287^{**}	0,08	0,065	~ 30000
* – at pressure $11*10^9$ Pa ** – contain the transition temperature of tin from the semiconductor state to the metallic state (α → β)							

Another modification of carbon – graphite differs from diamond by the character of structure and significant conductivity. Graphite has layer structure; each atom in layer is covalently linked with three adjacent atoms of the same layer. One of four electrons for each atom is delocalized. These delocalized electrons cause the metallic nature of graphite conductivity. Layers linked between each other by van-der-waals forces (source of bonding type of Van-der-Waals force is polarizing effect caused by the influence of force fields moving valence electrons of another atom (molecules) in the force fields of moving valence electrons of other atom (molecules)), sharply decreases with distance. Thus, graphite is an example of complex substance with mixed bondings.

Silicon and germanium was prepared, and used not only in crystalline but also in amorphous state. Silicon and germanium are the main materials of semiconductor electronics and microelectronics. On the basis of these materials, especially silicon, produce the main classes of electronic semiconductor devices: diodes, transistors, photodetectors, solar energy photoconverters (solar cells) as well as integrated circuits – the basis of microelectronic and microprocessor devices. However, the "gap" of direct optical transitions in germanium and silicon eliminates the possibility of manufacturing of optical quantum generators on their basis. Silicon and germanium is produced in the form of single crystals, films and layered structures with wide nomenclature of the properties, and the production of semiconductor silicon is continuously growing. Silicon (purified significantly worse than semiconductor devices) are also widely used as alloying element in steel, especially in electrotechnical (transformer).

VB subgroup *elements* – phosphorus, arsenic, antimony and bismuth. In V group elements are implemented chemical bondings through the formation of p^3 –orbital, which, in accordance with rule of Hume-Rothery (2.3) lead to structures with coordination number Z_K=3, belonging to rhombohedral syngony. Crystal with Z_K=3 in particular, consisting of two-layer plates. Each atom has three nearest neighbors in adjacent layer of the same plates, with which it is linked by covalent bondings. Adjacent plates are interconnected by weak Van-der-Waals forces. Due to the fact that covalent bondings do not penetrate the entire crystal, elements of VB subgroup are more plastic than the elements of IVB subgroup.

The relationship between the position in the periodic table and properties of VB subgroup elements illustrates Table 2.5. Regularities in the bandgap change are similar to above described IVB subgroup elements. In addition, it is clear that p^3 bondings much weaker than sp^3 bondings.

VB subgroup elements are widely used in semiconductor electronics, on the other hand, as donor impurity in the elemental semiconductors like germanium and silicon, and the other – as major component of $A^{III}B^{V}$ semiconductor compounds and several others.

VI B subgroup elements – sulfur, tellurium, selenium. Chemical bonds are realized through the formation of p^2 orbitals, Z_K=2. Crystals of these elements consist of spiral chains or rings, in which each atom has covalent bonding with atoms of the same chain. Between each other chain linked by Van-der-Waals forces. Links in these crystals is even weaker than in the VB subgroup. The correlation between the value of E_g and the serial number is the same as in VB subgroup (see. Table. 2.5).

Table 2.5. Some properties of elementary semiconductors arranged in VB and IVB subgroups

element	Z	shortest interatomic distance, nm	T_m, K	E_g, eV, at 300 K
VB subgroup				
Phosphorus	15	0,34	–	1,5
Arsenic	33	0,25	1090[*2]	1,2
Antimony	51	0,29	903	0,11
Bismuth [*1]	83	0,31	544	0
IVB subgroup				
Sulfur	16	–	392	2,4
Selenium	34	0,23	494	1,6
Tellurium	52	0,29	723[*3]	0,3

[*1] bismuth – semimetal

[*2] at pressure ~ $3{,}6 \cdot 10^6$ Pa

[*3] for gray crystalline tellurium

VI B subgroup elements includes as main components $A^{II}B^{VI}$, $A_2^V B_3^{VI}$, $A^{VI} B^{VI}$ and etc. numerous semiconductor compounds. In addition, they are used as donor impurities in $A^{III}B^V$ compounds.

VIIB subgroup elements. Among the elements of this subgroup semiconductor is only iodine. In the solid state it has semiconductor properties, it realized p- bonding. Iodine crystals are composed of diatomic molecules bound by Van-der-Waals forces. Weak links explain the volatility of iodine.

Iodine is used as donor impurity doping in semiconductor compounds, and included as component in the compounds of A^IB^{VII} type.

Thus, in substances of VB, VIB и VIIB subgroups bondings are pronounced heterodesmical character. Atoms in some directions or planes are linked by strong covalent, while others – weak van-der-waals chemical bonding. This greatly affects to the behavior of these substances. Since the strength of the van-der-waals bondings weaker by 1-2 orders of covalent bonding strength (0.02 – 0.2 eV and 2 – 3 eV, respectively), the first destroyed by heating the van-der-waals bondings (the so-called process of sublimation) and at higher temperatures – the covalent bonding (dissociation). Solid during sublimation decomposed into atomic groups, molecules, upon dissociation – into atoms.

Ease of sublimation processes explains high volatility of most substances of V – VI groups. This circumstance makes it difficult to obtain semiconductor compounds formed with the participation of these substances ($A^{III}B^{V}$, $A^{II}B^{VI}$ class compounds and etc.) of strictly specified composition.

Chapter 3

PHASE EQUILIBRIUM IN SEMICONDUCTOR, DIELECTRIC AND METAL SYSTEMS

§ 1. Main aspects of the thermodynamics of phase equilibrium

Real materials are compositions formed by several chemical elements.

Semiconductor compound composed of two or more elements. Semiconductor thermoelectric materials include 4-5 (or more) elements, dielectric phase – 4-8 elements, etc. Modern metal alloys are often more complex compositions. Even very pure crystals of germanium and silicon always contain background impurities.

Interaction of chemical elements forming this alloy can be very difficult. The result of interaction depends on the concentration of the elements, their nature and also external parameters of temperature and pressure.

In the result of various elements interaction emerge chemical compounds and solutions, aggregate states, physical and chemical properties of which depend from composition, pressure and temperature.

Before considering ways to describe the results of chemical elements interaction, we introduce the necessary thermodynamic concepts.

Material system – part of the space allocated for various signs and filled with substance or substances.

The space, which is separated from the material system, called as **external environment** to the system.

The thermodynamic system – is material system, between the parts which can exchange energy.

Physico-chemical system – the thermodynamic system, between the individual parts which can be exchanged substance. For example:

1) The system of two bodies – vials and placed in it melt. The melt do not wet the wall of ampoule and between the melt and

ampoule no chemical interaction. The combination of these bodies (ampoule with substance) are 1 thermodynamic and 2 physical-chemical systems (ampoule and melt).

2) The set of two bodies: crystal in contact with the melt of the same substance – one physical and chemical system. One substance in the solid and liquid phases (during crystal growth).

Closed system – a system that can not exchange matter with the external environment.

Adiabatic system – a system that can not exchange energy with the external environment.

Insulated (closed) system – a system that can not exchange neither substance nor energy with the environment.

Open system – a system that can exchange either energy or matter with the environment. Production of metals, semiconductors and dielectrics – are open system.

System may be in equilibrium and non-equilibrium states.

The equilibrium state of system – unchangeable (constant) time system state. The constancy of state is not supported by the occurrence of any external to the process of system.

Heterogeneous system – is a physicochemical system, within which there is an interface (or surface) that separating one from the other parts of the system in which occur abrupt change at least one of the system properties. Example: monocrystal in contact with the melt.

Homogeneous system – a physical-chemical system within which no interface on which there would be abrupt change at least one of the properties of the system. Example: monocrystal, polycrystal.

Substances which form the system called as **components of the system.** Components in the system presented in various phases.

Phase – a homogenous system in equilibrium or set of homogeneous parts in heterogeneous system in equilibrium. **In the other words, it is** a homogeneous part of the system, limited from other parts of the system by interface, transferring through which the properties changes abruptly.

Examples: 1) single phase system- quartz crystal. And also a lot of quartz crystals.

2) 2-phase system – a) crystal of Si, comprising the inclusion of SiO_2;

b) ice crystal in water and many ice crystals in water.

The process of transition from liquid or gaseous state to solid, at the result of which forming the crystal lattice, and occur crystals called as ***crystallization.***

What explain the existence of liquid at one temperature, and at other temperatures of solid state and why the transformation occurs at well-defined temperatures?

In nature, all spontaneously occurring conversions, and consequently crystallization and melting due to the fact that the new state in new conditions is energetically more stable, has lower energy content. We can say that the more free energy of the system, the system is less stable, and if it is possible, the system transferred into state where the free energy is less.

For solids the most important feature of phase is its crystal lattice (atomic structure). Each phase has its own, only her inherent crystal lattice, which differs from the other phases by type or size of the unit cell.

Allotropy and polymorphism – different structures of the same element with essentially same binding energy.

Binding energy – the energy necessary for the separation of solid bodies into individual atoms, molecules or ions (depending on the composition of solid). E_b – binding energy is equal to the difference between the potential energies of isolated atoms and related systems, net of kinetic energy, which, according to the uncertainty principle, should be determined by the localization of nuclei and electrons of the outer shell.

Different allotropic modifications of the same chemical element (α- and β- tin, α- and γ-iron, etc.) are different phases; phases are compounds, solid solutions on the basis of elements or compounds.

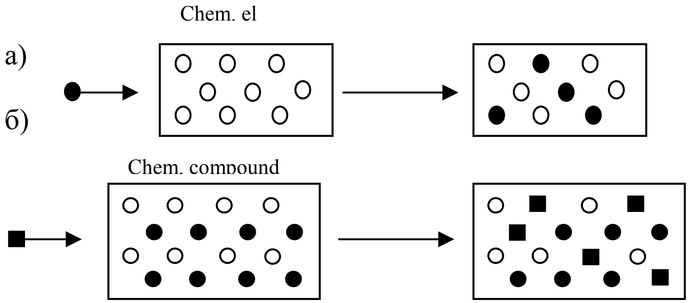
In solid, you can specify three basic types of possible phases of the interaction of diverse components:

1) compounds;
2) solid solutions;
3) mechanical mixture.

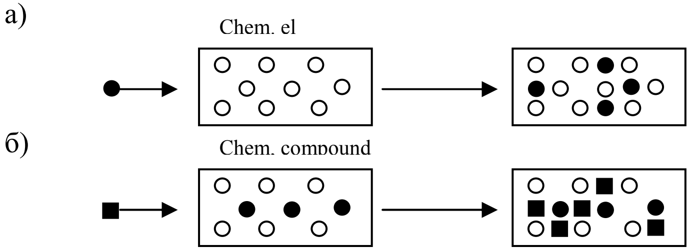
Compounds. Feature that this phase belong to chemical compounds, is the difference of the crystal lattice from lattice elements of which it is formed.

Solid solutions. Feature of the formation of solid solution is the conservation of the lattice-type component – solvent, but with different dimensions of the unit cell. In the result could form solution with limited and unlimited solubility with different temperature dependence of the solubility limit. On the basis of solvent (chemical element), there are 2 types of solid solutions:

1) substitutional solution – atoms of dissolved elements occupy the positions of solvent atoms in the lattice point (replaced them).

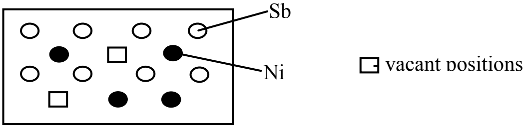


2) interstitial solution – atoms of dissolved elements occupy interstitial positions (interstices) in the lattice of solvent, penetrating between the atoms of the latter. In this case, the dimensions of soluble atoms must be smaller than the interstices.



3) omission solution- one of the components forming compound is present in amount exceeding definable relationship (as would be dissolved in the compound of stoichiometric composition), but it takes in the lattice of compound inherent position and corresponding part of the position of another element remains unoccupied (vacant).

Omission solution



Stoichiometric compound (stoichiometric composition) – is chemical compound in which the valence of incoming component completely satisfied (no outstanding bondings).

Mechanical mixtures are formed from two or more phases. Phase forming mixture can be elements or compounds. However, as rule, they are solid solutions.

Forming of mechanical mixture occurs:

1) due to discharge of second phase from supersaturated solid solutions.

2) due to eutectic or eutectoid transformation.

The eutectic (gr. Eutektos – easy melting):

1) granular mixture of solid solutions simultaneously crystallize from the melt at temperature lower than the melting temperature of individual components;

2) liquid melt or solution, from which such crystallisation is possible:

eutectic transitions:

1) liquid phase $\rightleftarrows s_1 + s_2$

eutectoid transitions

2) $s_1 \rightleftarrows s_2 + s_3$

Solid crystalline phase may be obtained as single crystals, polycrystals and amorphous solids, representing set of grains (or crystals). Differently oriented in space polycrystal crystallites are separated from each other by the interfaces – the grain boundaries – thickness of several interatomic distances. The grain boundaries are not the interphase boundaries in polycrystals.

System components (K) – chemical elements and compounds from which the phase can be constructed, that is, as the components may perform individual substances (chemical elements) or compounds.

Number of components (K) – minimum number of individual substances of which may be constructed any phase of the system. In general, the number of components can be less than the number of chemical elements contained in the composition of phase.

Example: Compound of InAs and InP can form between each other continuous series of solid solutions: InAs – InP. Chemical elements – 3, components of the system -2- both compounds, as in any condition of alloy the total atomic percentage (As + P) = In.

It should be noted that the physical-chemical system formed by the components is not adequate concepts.

In the **one-component** systems are implemented phase, with constant chemical composition, which can be in various aggregate states as: solid, liquid and gaseous. The length of the existence region of particular phase or existence region of different phases of single-component system is determined by external parameters like temperature (T) and pressure (P).

In the **multi-phase** systems are phases implemented as constants (individual substances) and, mainly, variables in chemical composition (solution) such phases are realized in solid, liquid or gaseous state. The length of the existence region of constant composition phase is determined by the values of the external parameters (P and T).

The length of the existence regions of variable composition phase, as well as the region of different phase coexistence, defined as the values of the external parameters (P, T) and the composition of phases.

Condensed systems – solids and liquids away from the critical point (the phase transition point). Solids and liquids are characterized by the compressibility of million times less than gas. Fundamental differences and character of the thermal motion of particles in condensed medium- is oscillating, in gases – forward.

Depending on the temperature and pressure (for metals mainly on the temperature, P-sonst) all substances can be in four aggregate states: plasma, gaseous, liquid and solid.

Plasma – an ionized gas, in which volume density of positive and negative electric charges are equal.

In gaseous state atoms are practically do not connected with each other and move randomly in space.

In the liquid state atoms are poorly connected to each other, there is short-range order, the material takes the form of the vessel, parts are easily separable from each other.

In the solid state atoms interact with each other by certain law, the structure has both short-range and long-range order, atoms form crystal lattice of species.

The transition between aggregate states is accompanied by the change in free energy:

$$F = U - TS \tag{3.1}$$

where U – internal energy;

T – temperature;

$S = \frac{q}{T}$ – entropy.

There are 5 types of condensed systems:

1. liquid
2. glass
3. amorphous
4. liquid crystals
5. crystals

Liquids – equilibrium, isotropic structurally disordered systems with fluidity, i.e., easily change its shape.

Glass – quasi-equilibrium, isotropic structurally disordered systems with mechanical properties of solids.

Amorphous – strongly non-equilibrium, isotropic, structurally disordered systems obtained under extreme conditions.

Liquid crystals – equilibrium, anisotropic, partially structurally ordered systems with high fluidity.

Crystals – equilibrium, anisotropic, structurally ordered systems (characterized by long-range order and translational symmetry).

§ 2. Phase equilibrium. The rule of phase. Gibbs Law

In single-component or multi-component systems can be realized state, when in equilibrium are several phases. This condition is called **heterogeneous equilibrium.**

Heterogeneous is equilibrium in system consisting of F-phase and K components realized under the following conditions:

$$K-\text{lines}\;\overbrace{\left\{\begin{array}{l} T_1=T_2=T_3=\ldots=T_f \\ P_1=P_2=P_3\ldots=P_f \\ \mu^1{}_1=\mu^1{}_2=\mu^1{}_3=\ldots=\mu^1{}_f \\ \mu^2{}_1=\mu^2{}_2=\mu^2{}_3=\ldots=\mu^2 \\ \\ \mu^\kappa{}_1=\mu^\kappa{}_2=\mu^\kappa{}_3=\ldots=\mu^\kappa{}_f \end{array}\right\}}^{\text{F column}}\;(K+2)-\text{lines} \qquad (3.2)$$

where the superscript *K*- is the number of components, the lower *F* – phase number, $\mu^\kappa{}_f$ –the chemical potential of the *K*- component in the *F*-phase. The concept of chemical potential is central in phase equilibrium.

The system of equations (3.2) consists of (*K*+2) lines and *F* columns. In the first two lines contain the condition that temperature of each phase and pressure of each phase are the same throughout the system. The following K lines fixed position that the chemical potential μ_i of given component in all phases are same.

Chemical potential of i-th component is called the work spent to increase the number of particles of the i-th grade at system to one unit at constant all the other variables that determine the thermodynamic potential (particle means atoms, molecules).

Depending on the conditions in which phases, for describing used following thermodynamic potentials:

G –isobaric-isothermal potential (Gibbs potential),

F –free energy (Helmholtz energy) or isochoric-isothermal potential,

U – internal energy of the system,

H – enthalpy of the system (the heat of fusion, crystallization).

$$G = H - TS \text{ или } G = PV - TS, \qquad (3.3)$$

where S – entropy.

The chemical potential is a partial derivative of thermodynamic potentials by the number of particles of i-th component in phase:

$$\mu = \left(\frac{\partial G}{\partial N}\right)_{P,T} = \left(\frac{\partial F}{\partial N}\right)_{T,V} = \left(\frac{\partial H}{\partial N}\right)_{S,P} = \left(\frac{\partial U}{\partial N}\right)_{S,V} \qquad (3.4)$$

where N – number of particles in single-component phase.

In the analysis of heterogeneous equilibrium is important to know how many phases are in equilibrium, and how much number of system parameters can change independently without affecting number of phases in equilibrium. The answer to this question is given by the law, opened in 1876 by Gibbs and known as ***"phase rule"***.

As the system parameters in one-component systems are the temperature (*T*) and pressure (*P*), in multicomponent systems – *T*, *P* and the concentration of the components in each phase – *X*. In each phase consisting of *K*- components, the number of variables of concentration equal to: $(K-1)$, so how $\sum_i X_i = 1$. Example: the two-component system $X_A + X_B = 1$, $X_A = 1 - X_B$.

Such external parameters such as the characteristics of fields in which there are phases in the analysis of physical and chemical equilibria are usually not included in the assumption that they remain constant.

The number of freedom degree or variation of the system- C – number of system parameters that can be changed without changing the number of phases in equilibrium. The value C is equal to the number of independent variables; i.e. minimum number of variables, which are selected and uniquely sets the other parameters. Thus, the value of C is equal to the difference between the total number of variables of system and the number of equations. The total number of variables in the system (3.2): $F(K-1)+2$.

Variation of the system consisting of K – components and F – phase when the external parameters are only P and T is equal to:

$$C = [(K-1)F + 2] - [K(F-1)]$$

The phase rule (or Gibbs law) provides quantitative relationship between the freedom degree of the system and number of phases and components:

$$C = K - F + 2 \tag{3.5}$$

mathematical notation of ***phase rule*** or **Gibbs law**, where C – is the number of freedom degrees, i.e., the number of external (temperature and pressure) and internal (concentration) factors that can change without changing the number of phases;

K – number of components in the system;

F – the number of phases.

In those cases where the number of external parameters is decreased to one unit (P = const and T = const), the phase rule is written as follows:

$$C = K - F + 1 \tag{3.6}$$

In those cases where the number of external parameters is zero, i.e. the pressure P and temperature T – constant (P = const and T = const), the phase rule is written:

$$C = K - F \tag{3.7}$$

Example: If C = 0, then any changing in temperature causes change in the number of phases; if C = 1, it is possible changing of temperature without changing the number of phases.

In the liquid state:

F = 1 – one phase;

K = 1 – one component (pure metal);

C = 1 – 1 + 1 = 1 – you can change the temperature without changing the aggregate state.

The freedom degree for the alloy at the time of crystallization:

F = 2 – two phases (liquid +crystals);

K = 1 – one component (pure metal);

C = 1 – 2 + 1 = 0 – equilibrium at strictly definite temperature (T_m).

The number of relationship equations between variables (the concentrations of the components in phase) is prepared based on the requirements of the same chemical potential of component in all phases of the system (in equilibrium), since the chemical potential of component in phase depends on the concentration of the component. This dependence is expressed by the equation:

$$\mu=\mu_0+kT\ln(\gamma X) \qquad (3.8)$$

where μ_o – chemical potential of component in the standard state (under normal conditions), γ – activity coefficient of the component in phase, k –Boltzmann constant, X – the concentration of component in phase.

Therefore, under conditions of phase equilibrium occurs equilibrium redistribution of components between the phases.

<u>Consider an example:</u> in system consisting of 2 components (K=2), in two-phase equilibrium condition (F=2) for each of the components (e.g., for component 1) is realized equation:

$$\mu_1^1 = \mu_2^1 \qquad (3.9)$$

$$\mu_{01}^1 + \mathrm{kT}\ln(\gamma_1^1 X_1^1) = \mu_{02}^1 + \mathrm{kT}\ln(\gamma_2^1 X_2^1) \qquad (3.10)$$

$$\ln\left[\frac{\gamma_1^1 X_1^1}{\gamma_2^1 X_2^1}\right] = (\mu_{02}^1 - \mu_{02}^1)/\,\mathrm{kT} \qquad (3.11)$$

$$k_0 = \frac{x_1^1}{x_2^1} = \left(\frac{\gamma_2^1}{\gamma_1^1}\right)\exp\left[\frac{\mu_{02}^1 - \mu_{01}^1}{kT}\right] \qquad (3.12)$$

where $k_0 = \frac{x_1^1}{x_2^1}$ – ***equilibrium distribution coefficient***. In this case, the distribution coefficient of component 1 between phases 1 and 2 (for example $\frac{x_1^1}{x_2^1}$ – – the ratio of concentration in the phase 1 and phase 2 of the component 1 (the ratio of the concentrations of component 1 in solid and liquid phase). Thus, the distribution of the components (more accurately distribution of components concentration) between the phases is characterized by ***equilibrium***

distribution coefficient, the value of which is derived from the equations of bonding type (3.12).

In general case, the number of bonding equations for heterogeneous equilibrium in multiphase system is obtained from κ of lower lines of system (3.2) and it is equal to: $K(F-1)$.

To analyze the phase equilibrium phase law usually used in the form of (3.5; 3.6; 3.7) depending on conditions, in which located system.

§ 3. Construction methods of phase equilibrium diagrams

The phase equilibrium can be described by both analytically and graphically. For graphic description used ***equilibrium phase diagrams*** (EPD) or ***phase diagrams*** (PD), which are sometimes called *diagram of the system state.*

EPD of single component system is geometric representation of phase states, which are realized in single component system under various external parameters. FID component system built in the pressure-temperature coordinate ($P-T$).

EPD of multicomponent system ($K>1$) is geometric image of the phase states (equilibria and transformation phase), realized under various parameters in the result of components interaction of the system. EPD of multicomponent system built in the coordinates of $P-T-X$, where X –concentration of the component.

Each point of EPD characterize the physico-chemical parameters of systems resulting from the interaction of the components making up the EPD.

EPD can be 2-dimensional, 3- dimensional, etc. With using EPD for the given conditions can determine:

1) number of phases in the system;
2) relative amount of each phase;
3) composition of each phase and its nature (i.e., pure component, solution, compound etc.)
4) character of phase transformations.

It will be appreciated that the EPD without special explanations does not provide information about atomic structure of phases and their crystal lattice. EPD can be considered as fully reliable only after using X-ray structure analysis (XSA) deciphered the atomic structure of each phases in the system.

The main method of constructing EPD – method of physical and chemical analysis, foundations of which were developed by academician N.S. Kurnakov (Kurnakov IGIC RAS). The basis of physical-chemical analysis is the study of functional relationship between the physical properties values and *T*, *P*, *X* parameters. Knowledge of these relationships allows to set the physical-chemical nature of the phases and boundaries of their existence. Physical properties are determined from the dependence of f(T), f(P), f(X).

Experimental methods used to build the EPD.

1. Thermographical analysis (differential-thermal analysis – DTA).
2. X-ray microanalysis.
3. X-ray structure (X-ray-graphical) analysis (XSA, XGA). It is also used electron microscopy (EM) and neutron radiography (NR).
4. Dilatometric analysis (measurement of density), and others.

The essence of thermographical (DTA) and dilatometric methods of construction of EPD is that to the alloy with such composition **temperature of phase transformation (the "critical points") determined *by abrupt change in enthalpy H (H – melting heat) or volume (V)*** of the system on dependences $T = f(t)$ – time or $T = f(V)$ in the process of cooling or heating alloy. I.e. identify the critical points for the series of alloys, and then build all diagram. These methods are determined by the phase transitions of I-kind, as in any other phase transformations of thermodynamic potentials (G, F, H) changing without jump, because at equilibrium transformation temperature their values for old and new phases are equal.

Phase transitions. Phase transitions can be I-st and II-nd kind. **To first order** phase transitions include transitions in which *G*, *F*, *H* thermodynamic potentials are changed without jump, but abruptly changed at the phase transition temperature of the first (partial) derivatives from thermodynamic potentials (at this case majority of transformations is allotropic (melting, etc.))

$$\text{(G=H-TS=PV–TS):}\frac{\partial\left(\frac{G}{T}\right)}{\partial\left(\frac{1}{T}\right)}=H\;;\qquad \left(\frac{\partial G}{\partial P}\right)_T=V\;;$$

$$\left(\frac{\partial G}{\partial T}\right)_P=-S \tag{3.13}$$

That is first kind phase transitions that accompanied by abrupt changing in enthalpy (*H*), volume *(V)* and entropy *(S)*.

Phase transitions of II-nd kind

In some rarer phase transitions from one state to another:

ferromagnetic $\rightleftarrows$ paramagnetic;
superconducting $\rightleftarrows$ non-superconducting;
ordered $\rightleftarrows$ disordered.

The first derivatives changed continuously, but changed abruptly the second derivatives of thermodynamic potentials.

$$\left[\frac{\partial^2\left(\frac{G}{T}\right)}{\partial\left(\frac{1}{T}\right)^2}\right]_P=\left[\frac{\partial H}{\partial T}\right]_P=c_p\;;\quad \left[\frac{\partial V}{\partial P}\right]_T=\beta V\;;$$

$$\left[\frac{\partial S}{\partial T}\right]_P=\frac{c_P}{T} \tag{3.14}$$

where β – compressibility coefficient, (for solids $c_P \approx c_V$). Phase transformations, accompanied by abrupt changing in the second derivatives of thermodynamic potentials are called phase transitions of II-nd kind.

At phase transitions of the second kind first derivatives of thermodynamic potentials change continuously, but abruptly changed the second derivatives.

A common method of physical-chemical analysis is building diagram of "structure – property". For this composition we can build such diagram:

Temperature – property;
Pressure – property.

As shown by N.S. Kurnakov and confirmed by huge factual material, based on geometric analysis of diagrams "structure – property" (or, in general case, " variable factor – property") existed two general principles:

1) principle of continuity
2) principle of conformity.

According to the principle of continuity: at continuous change in the chemical composition (or other variable factors – *T*, *P*), is not accompanied by changing in the phase composition (number of phases), continuously and smoothly changing of system properties.

According to the conformity principle, each phase and each phase equilibrium corresponds definite geometric image of the phase equilibrium diagram (EPD). The conformity principle more "capacious" principle, than the principle of continuity.

As part of the conformity principle can also be formulated important provisions, which facilitate the analysis of phase diagrams:

1. All lines of double diagrams and surface of triple diagrams limited phase region, the number of phases which differ to one unit.
2. All sloped lines (surface) is characterized limited concentration of the primary dopant in the phase. The slope of line (surface) characterizes the temperature dependence of the concentration limits.
3. Dimensionality of geometric elements that characterize particular phase equilibrium responsible to variance (C) corresponding to the phase equilibrium. Example: points on the diagram characterize phase compositions undergoing monovariant transformation.
4. For alloy of any composition intersection of its with ordinate (y) lines (surfaces) in the diagram during the cooling or heating process is accompanied by changing of phase composition.

In Table 3.1. specified properties of materials commonly used in the construction of the EPD.

To obtain reliable conclusions about the structure of EPD should study not one, but also combination of several physical properties.

An important method for determining the number of phases (F) and their amount (concentration) is metallographic analysis.

Table 3.1. Properties of materials most commonly used in the construction of phase equilibria diagrams

Class of used properties	Quantity that characterize property	Unit of measurement
Thermal	Heat of the phase transition Heat of formation Heat capacity	*J/mol* ----------- *J/(kg·K)*
Electrical	Electrical resistivity Thermoelectric power	*Ohm·sm* *mV/K*
Magnetic	Magnetic permeability	-----------
Volumetric	Density Coefficient of thermal expansion	g/sm^3 K^{-1}
Force of bondings	hardness (microhardness)	*MPa*

In the analysis of the EPD (state diagrams) are primarily used Gibbs phase rule (C-variance of system, or the number of freedom degrees, K – the number of components): $C = K - F + 2$.

a) If $C = 0$ – system is non-variant. The system can only exist under constant conditions. Change at least one of the parameters of system will cause change in the number of coexisting in equilibrium phases (F).

b) If $C = 1$ – system is multivariant (singlevariant). However, only one parameter can be changed without changing the number of simultaneous equilibrium phases, etc.

c) If $C = 2$ – divariant system (dualvariant). Two parameters can be changed without changing the number of simultaneous equilibrium phases.

Example:

Task: Consider the crystallization of silicon (Si) at P=const from its liquid melt, heated to 1500°*C*. $T_{mSi} = 1412°C$. Determine the value of C for different phase regions.

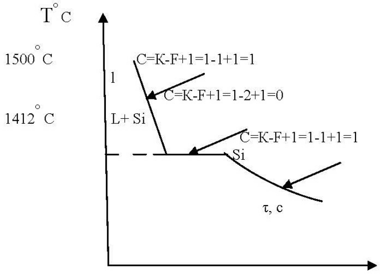
Solution: The number of external independent variables – (temperature) is equal to – 1, the number of components – 1. Upon cooling the melt from 1500° C to 1412° C system is single-phase. Then

$$C=K-F+1=1-1+1=1,$$

that is **temperatures in this range can be changed without changing the number of phases.** Upon reaching T=1412° C appears second (hard) phase, wherein

$$C=K-F+1=1-2+1=0,$$

that is, while there will be two phases, the system is non-variant. And the temperature will not fall until all liquid melt crystallized. This means that with the continued smooth decreasing of heater temperature in the physical-chemical system, the temperature will be maintained through **the provision of the crystallization heat.** In graph of $T=f(\tau)$ will be T=const area, whose length is equal to the time from beginning to end of crystallization (τ-time).



What keeps the system temperature of T=1412° C in conditions where the heat is continuously given to environment?

The source of maintaining the temperature is released crystallization heat.

In the case of transition of substance from one phase state to another is released into the external environment or absorbed from them additional amount of energy. This energy is called ***the heat of phase transition*** and is equal to the difference between the enthalpy of old and new phases.

Task. Consider crystallization of germanium (Ge) at P=const from its liquid melt, heated to 1200°*C*. T_m(Ge) = 940°*C*. Determine the value of *C* for the different phase regions.)

One should distinguish four possible cases of phase transitions (transformations):

1. During the transition from solid to liquid or vice versa generates heat melting or heat of crystallization:

Solid phase ⇄ liquid phase – heat of melting (crystallization)

2. During transition from one solid phase to another solid phase – generates heat recrystallization.

Solid phase ⇄ solid phase II – heat recrystallization

3. At the transition from solid state to gaseous state or vice versa generates heat of sublimation.

Solid phase ⇄ gas – heat of sublimation

4. During the transition from liquid to gaseous state, or vice versa released heat of evaporation.

Liquid phase ⇄ gas – heat of evaporation

For the case of 1, 3, 4 – characterized by significantly greater absolute values of thermal effects, compared with the case 2. In Table 3.2. shown the values of the heat of melting for some elements.

Table 3.2. The values of the heat of melting for some elements

Element	H_m, kJ/mol	Element	H_m, kJ/mol
Fe	15,50	Ge	37,08
W	35,28	Te	17,70
C	138,27	Se	6,70 ± 1,68
Si	49,86	S	1,72

§ 4. T – X diagrams of phase equilibrium of binary systems with unlimited solubility of the components

T–X state diagrams of binary systems built in the coordinates of the temperature (*T*) –concentration (*X*). The concentration usually lay in atomic percentage (at.%) and sometimes used percent by weight.

For systems in which one component is semiconductor (chemical element or compound), together with the diagrams constructed in conventional scale, also built diagrams in which in the region adjacent to semiconductor, the concentration of doping component in at.% applied on logarithmic scale (Figure 3.1 в.), or build separate part of the diagram, adjacent to the semiconductor component, putting the concentration of 2nd component in atoms per cubic centimeter also in logarithmic scale (Figure 3.1. a).

This is because the carrier concentration in semiconductor is measured in electrons (or holes) per cubic centimeter, and in those cases where dopants are providers of charge carriers, it is comfortable to measure carrier and impurity concentration in the same units.

Furthermore, limit solubility of impurities in semiconductors, is generally very small ~(0,1– 0,01) % atm. and actually used doping concentration of (10^{14}–10^{19}) atoms/cm^3, i.e., (10^6–10^{-1}) % at. In these conditions it is important to show phase regions in the diagrams in which components concentration in the low concentration regions varies by one order of magnitude. The logarithmic scale used when in normal scale concentration range is less than 0.1% and merges with the ordinate axis.

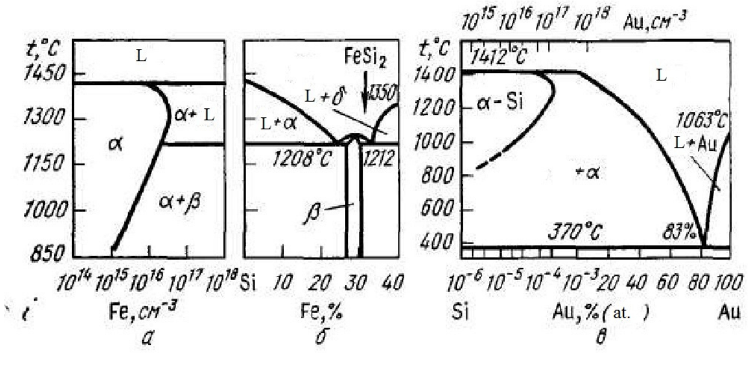


Figure 3.1. – *T–X* phase equilibrium diagrams of two-component systems with limited solubility of component *а* – concentration in atoms per cubic centimeter; *б* – in atomic percent in linear scale; *в* – in atomic percentage; in the region adjacent to semiconductor, atomic percentages of dopant component plotted on logarithmic scale

Calculation of components concentrations from one scale to another (from at.% to % by weight) carried by the following formula:

$$X_1\%(at.) = \frac{X_1\%(by \cdot weight)/A_1}{[X_1\%(by \quad weight)/A_1]+[X_2\%(by \quad weight)/A_2]}100 \tag{3.15}$$

$$X_1\%(by \quad weight) = \frac{X_1\%(at.)A_1}{X_1\%(at.)A_1 \quad + X_2\%(at.)A_2}100 \tag{3.16}$$

$$X\%(at.) = \frac{X \quad atom/см^3}{N}100 \tag{3.17}$$

$$Xat./см^3 = \frac{X\%(at.)N}{100} \tag{3.18}$$

Где X_1 % (at.) – atomic percentages of 1 and 2 components
X_2 % (at.)
X_1 % (by weight) – percentages by weight of 1 and 2components
X_2 % (by weight)

A_1 – atomic masses of 1 and 2 components
A_2

X_{at/sm^3} – (usually write $X_{sm}^{-3)}$ number of impurity atoms in the 1 sm^3

N – total number of atoms in the 1 sm^3

$N=\frac{n}{V}$, where n – number of atoms in the lattice, which are belong to one quantity of one unit cell;

V – unit cell volume.

Task. Calculate the number of atoms per one unit cell quantity in the Bravais lattice.

In the diagram of phase equilibrium (PED) represent phase regions separated from one of another by diagram lines (Figure 3.2).

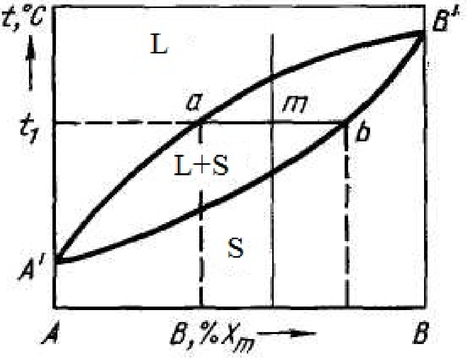


Figure 3.2. – Typical phase equilibrium diagram of *A–B* binary system with unlimited solubility of components in the liquid (*L*) and solid (*S*) states. In the two-phase region shown *ab* conode.

Any point on diagram can be viewed as ***figurative point of the alloy,*** describing its state. Projection of figurative point on the *X*-axis indicates the composition (concentration) of alloy. Projection of the same point on axis *T* – temperature axis at which this alloy is considered. Position of figurative point also indicates to the phase composition of alloy at this temperature.

a and ***b*** points- figurative points of the phases, ***m*** point- figurative point of alloy. If figurative point is **in the single phase region,** the phase composition matches with the alloy composition. If figurative point is within the **two-phase region,** the phases composition in equilibrium at given temperature is determined by ***conode*** passing through this point. ***Conode*** called a line segment, drawing at constant temperature (i.e., in isotherm) and enclosed within the two-phase region. **Conode** crosses the boundary of this region at points on the conjugate lines and figurative point phases which are in equilibrium at given temperature (a and b points), i.e. tie conode connecting points, characterized the composition of phases in equilibrium ***(ab – conode).*** *A*' and *B*' points on EPD correspond to the melting temperature of the pure binary system of *A* and *B* components, respectively.

A'*aB*' line, above which all alloys is in liquid state is called ***the liquidus line*** (*L*): is the geometric locus of points characterizing the composition of liquid (*L*) phase (solution) of limiting concentration and temperature dependence of this concentration.

A'*bB*' below line in which all alloys in the solid state is called ***the solidus line*** (*S*): it is the geometric locus of points that characterize the composition of the solid (*S*) phase (solution) of limit concentration and temperature dependence of this concentration.

The region between the solidus and liquidus lines – two-phase coexistence region of the liquid and solid phases (solution).

The quantitative ratio of the phases in equilibrium at given temperature is determined by the **lever rules:** *the ratio of the mass or volume amounts of Q-phases are in equilibrium at given temperature is inversely proportional to the ratio of conode segments, concluded between the figurative point of alloy and the figurative points of the respective phases.*

Example:

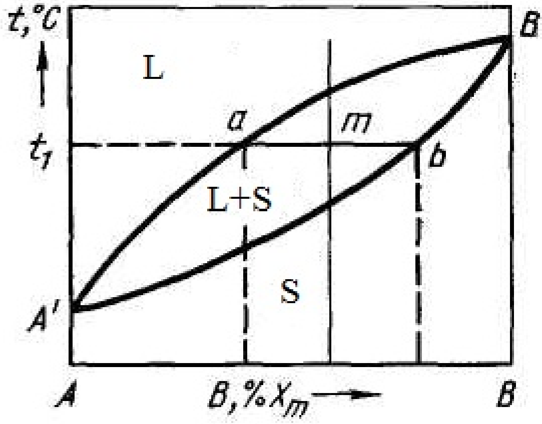


Figure 3.3. – Phase diagram with unlimited solubility of components in the solid and liquid states

At temperatures t_1 alloy composition x_m consists of two phases: liquid phase composition ***a*** (with concentration x_a) and solid phase composition ***b*** (with concentration x_b).

The proportion of the phases equal to:

$$Q_{L(a)}/Q_{S(b)} = mb/(ma) \qquad (3.19)$$

Where $Q_{L(a)}$ – composition of the liquid phase (X_a)

$Q_{S(b)}$ –solid phase composition in the ($X_в$)

If you know **the total mass** or **volume of alloy** Q_{alloy}, the absolute **amount** of liquid Q_L and solid Q_S phases determined from the following relationships:

$$Q_{L(a)} = Q_{ALLOY}\, mb/(ab) \qquad (3.20)$$

$$Q_{L(b)} = Q_{ALLOY}\, ma/(ab) \qquad (3.21)$$

Task. To determine the variance of *C* system (Fig. 3.1) for: a) the pure *A* and *B* components at the melting temperature; б) alloys are in single phase regions (liquid and solid); в) alloys are in two phase region.

Consider, as example crystallization of one from the real two component alloy system with unlimited solubility – Ge–Si alloy, containing 70% Si (Fig. 3.4).

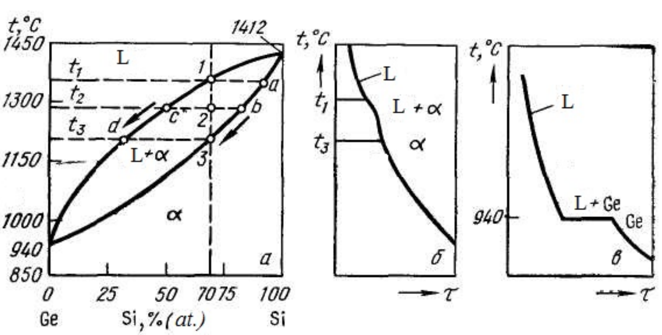


Figure 3.4. – Phase diagram of Ge- Si system (*a*) and cooling curves of the alloy of 30% Ge + 70% Si (*б*) and pure germanium (*в*).

To $t \geq t_1$ temperature X alloy composition is in the liquid solution state (*L*) and at cooling does not undergo phase transformations. Starting from t_1 temperature liquid solution is supersaturated with silicon and from liquid solution starts to separate solid **solution α,** where concentration of Si is larger than in original *L*, at the result melt is depleted by silicon. The first evolved **α crystals** have a composition corresponding to the **figurative point a,** i.e. 90% Si and 10% Ge. During cooling from t_1 **to** t_2 subsequent crystallization of the alloy occurs, during of which the amount of liquid phase is reduced, while solid increases. At $t = t_3$ disappear last drops of liquid melt.

Proportion of liquid and solid phases coexisting at any given temperature is determined by the lever rule. Thus, at temperature t_2

$$Q_S/Q_L = (2 - c)/(2 - b) \tag{3.22}$$

Furthermore, during the crystallization from t_1 to t_3 changed the composition of the liquid and solid phases. If the process occur with very slow velocity- so that all conversions completed in time in accordance with the phase diagram, the liquid phase composition varies over the liquidus line from point ***1 to point d***, and the solid composition- on the solidus line from point ***a to point 3,*** as indicated by arrows.

Both phases – disappears during crystallization, and the resulting – enriched during crystallization of the same component in the present case – Ge (germanium). This simultaneous enrichment of one and the same component is due to sharp decrease in number of simultaneous phase richer in this component (in this case, the liquid phase richer with germanium). Note that after the crystallisation process, passed under equilibrium conditions, there is only the solid phase, wherein its composition corresponds to the composition of the liquid solution (in the example is solid solution containing 70% Si).

Conditions of EPD realization with unlimited solubility. *A – B* dual systems*,* A and B components which are infinitely dissolved in each other in the liquid and solid states, may be formed by chemical elements and compounds. At the same time, both components must be:

a) have the same type of chemical bonding;

b) have the same type of crystal lattices;

c) unit cell parameters (or atomic radius) should not differ (*Δa*, *ΔR*) than at (10-15)%;

d) have similar potential relief of the crystal lattices of component. Such solutions are isovalent (with the same valence) substitution solutions (Table. 3.3)

Table 3.3. Dual system (metal and semiconductor) with unlimited solubility of the components

Solid solutions	*Components*	*Structure*	*Δa or ΔR, %*
Metallic	Au-Cu	*FCC*	11,2
	Ag-Cu	*FCC*	11,3
	Au-Pd	*FCC*	5,0
	Ni-Cu	*FCC*	3,0
	Fe-Cr	*BCC*	9,9
	Mb-W	*BCC*	9,9
	V-Ti	*BCC*	2,0
	Ti-Mo	*BCC*	5,0
Semiconductor	Ge-Si	*Diamond*	10,4
	InAs-InP	*Blende*	3,2
	GaAs-GaSb	*Blende*	8,0
	GaAs-GaP	*Blende*	3,0
	GaAs-InAs	*Blende*	8,0
	Bi_2Te_3-Bi_2Se_3	*Tetradymite*	8,0
	Bi_2Te_3-Sb_2Te_3	*Tetradymite*	8,0

From elementary diamond-like semiconductors equilibrium phase diagram with unlimited solubility form only silicon and germanium. They fully meet the requirements listed above. Silicon and carbon (diamond) meet the requirements of chemical nature and type of lattice, but differ greatly on the size of tetrahedral covalent radii (R_{Si} = 0,117 nm, R_C = 0,077 nm; $\Delta R/R_{Si}$ = 36%). In this connection, the solubility of carbon in silicon is not more than one hundredth of percent, and silicon in carbon is less.

Task. Define FCC, BCC, diamond lattice, sphalerite, tetradymite.

Application of solid solutions with unlimited solubility. Unlimited solubility – is very common feature among semiconductor compounds. They form together so many classes of $A^{III}B^{V}$, $A^{II}B^{VI}$, $A_2^{V}B_3^{VI}$ and etc. compounds (See. Table. 3.3). Such solid solutions are widely used. This is facilitated by the fact that solid solutions of semiconductors, with unlimited solubility allows to obtain alloys with any values of bandgap, lattice period (interatomic distances), coefficients of thermal expansion and number of other parameters in the range between their values for initial components.

Periods of lattice changes in the first approximation, additively (Vegard's rule), other parameters – by more complex laws.

Solid solutions with unlimited solubility (metallic or semiconductor) are widely used:

1. *Au-Cu, Ag-Cu* – in contacts of devices;
2. *Cu-Ni* – in electro-vacuum devices;
3. *Fe-Cr* – in stainless steel alloys (vacuum systems, etc.);
4. *Mb-W, Mb-Ti, V-Ti* – refractory materials;
5. *Semiconductor solid solutions* – semiconductor thermoelements, microelectronics, optoelectronics. Considering the opportunities created by solid solution with unlimited solubility, establishing the dependence of their properties on the composition is an important task of material science.

§ 5. Construction and analysis of diagrams with unlimited solubility according to the data about change of the thermodynamic potential. Coefficient of distribution

As we know from thermodynamics, at constant temperature and constant pressure, that phase will be in equilibrium, for which observed isobaric-isothermal potential $G = H - TS$.

$H = U + PV$ и $G = U + PV - TS$

In particular, for solid phase: $U = U_0 + U_T + U_E$, where U_0 – potential energy of the lattice at T = 0 K; U_T –the energy of atoms thermal vibrations at given temperature; U_E –elastic energy of the lattice distortion due to dissolution of foreign atoms; P –external pressure; V – volume occupied by phase; S – entropy; T – the absolute temperature; N – phase enthalpy. Note that in general case, the equilibrium state of the system is determined by the minimum of thermodynamic potential (*G*, *U*, *H* or *F*), which describes its state upon selected variable parameters.

Entropy is always positive (S> 0) and increases with increasing temperature, so the temperature increases G decreases (Fig. 3.5 *a*); The curve *G(T)* is always facing upward convexity.

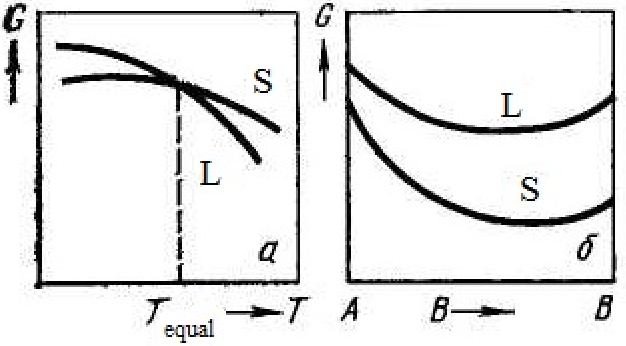


Figure 3.5. – Dependence of the isobaric-isothermal potential for liquid and solid phases of constant composition from temperature (*a*) and composition (*б*) for the liquid and solid phases of variable composition at *T*=const, in which in equilibrium state is the solid phase

If we compare the temperature dependence of ***G*** for two phases (liquid and solid Fig. 3.5), then the slope of curves will always be different because of the difference ***S***, so that the curves must intersect.

The slope of ***G* = *f*(*T*)** will be steeper in that phase, in which ***S*** is greater. Entropy of liquid phase is greater than the entropy of solid phase of the same composition, however the curve for liquid phase is reduced more sharply than in solid. The point of intersection T_{eq} corresponds to the temperature of the phase transformation. Below and above this temperature are stable different phases respectively having smaller value of ***G.***

Consider the concentration dependence of ***G*** in the system formed by ***A*** and ***B*** components. In the ideal case, when ***A*** and ***B*** components **do not dissolve into each other,** any alloy of this system is **mechanical mixture** of ***A*** and ***B*** components and

$$dG/dX_B^A = \overline{\mu_B} = tg\alpha \qquad (3.23)$$

thermodynamic potential of any system alloy is found by additivity rule. If component ***B*** is soluble in component ***A,*** then until composition corresponding to the **concentration limit (*X*$_{B\text{sat}}$)**, the dependence of ***G*** to concentration will be represented by continuous curve which is convex downwards, that is the equilibrium dissolution is associated with decreasing in ***G*** value of the solution.

Consider the shape of curve $G = f(X_B^A)$ near the component ***A*** (Fig. 3.5 *б*), e. g. in very dilute solutions region.

In this area dG/dX_B^A is equal to the tangent angle between the tangent to the curve *G=f*(*X*) and the axis ***X*** and hence chemical potential of component ***B*** in solution concentration X_B^A :

For ideal solutions $\overline{\mu_B} = \overline{\mu_B^o} + RT\ln X_B$ (3.24)

where $\overline{\mu_B^o}$ –chemical potential of **1 mole *B*** pure component (the value which depends only on the nature of component ***B);*** ***R*** – universal gas constant, equal to ***kN$_A$,*** where ***k*** –Boltzmann constant, ***N$_A$*** –Avogadro's number, so

$$dG/dX_B^A = \overline{\mu_B} = \overline{\mu_B^o} + RT\ln X_B \qquad (3.25)$$

For infinitely dilute solutions $X_B \to 0$ and respectively $\ln X_B \to -\infty$ and $tg\alpha \to -\infty$.

This means that the curve ***G=f(X$_B$)*** touched axis of ordinates, but it is especially important that at low concentrations of the components ***B*** in the derivative dG/dX_B^A ***is always negative.*** Therefore, **if impurity is dissolved in pure component, it is accompanied by decreasing in the isobaric-isothermal potential of the solution.** This means that in these cases the process must always proceed in the direction of contamination of the pure component.

This conclusion is important for the processes of producing high-purity metallic, semiconducting and dielectric materials and emphasizes the need to minimize the almost inevitable pollution of environment, crucible material, and etc. Note that in all known experimental studies it was found that there is always at least tiny solubility of the components in each other.

Thermodynamic characteristics of solutions. The length of the region of solution existence (both solid and liquid) is determined by number of its characteristics, including thermodynamic characteristics. Enter these specifications for two-component solutions. Most of the thermodynamic functions of the solution can be prepared by adding an additive thermodynamic functions of the components forming the solution. In particular, solution is formed only in the case when injected into solvent-additive decrease the isobaric-isothermal potential of solvent. Consider thermodynamic functions of 1 mole solution in its general form (index ***α*** –functions relating to the solution, ***o*** –functions relating to the pure components)

$$\begin{aligned} G^{\alpha} &= X_A G_A^o + X_B G_B^o + \Delta G_{см}; \\ S^{\alpha} &= X_A S_A^o + X_B^o S_B^o + \Delta S_{см}; \\ H^{\alpha} &= X_A H_A^o + X_B H_B^o + \Delta H_{см}; \\ V^{\alpha} &= X_A V_A^o + X_B V_B^o + \Delta V_{см} \end{aligned} \quad (3.26)$$

where the index **α** – labeled solution, index **0** – component G^{α}, G_A^o, G_B^o – isobaric-isothermal potential of solution and ***A*** and ***B*** components; $\Delta G_{см}$ – isobaric-isothermal potential shifting of the solution; ***X_A*** and ***X_B*** – concentration of ***A*** and ***B*** components in the solution; S^{α}, S_A^o, S_B^o – entropy of solution and ***A*** and ***B*** components; $\Delta Sshift$ – entropy of solution shifting; H^{α}, H_A^o, H_B^o – enthalpy of solution and ***A*** and ***B*** components; $\Delta H_{см}$ – enthalpy of solution shifting; V^{α}, V_A^o, V_B^o – volumes of the solution and ***A*** and ***B*** pure components; $\Delta V_{см}$ – volume of solution shifting.

Based on the 1st and the 2nd law of thermodynamics can be shown that

$$\Delta G_{см} = \Delta H_{см} - T\Delta S_{см} \tag{3.27}$$

If the description of thermodynamic functions of the solution to take into account only pairwise interactions between neighboring atoms, it can be shown that $\boldsymbol{\Delta H_{shift}}$ and $\boldsymbol{\Delta S_{shift}}$ equal to the following values:

$$\Delta H_{см} = X_A X_B \Omega_{AB} \tag{3.28}$$

$$\Delta S_{см} = -R(X_A \ln X_A + X_B \ln X_B) \tag{3.29}$$

where $\boldsymbol{\Omega_{AB}}$ –interaction parameter between ***A*** and ***B*** components in solution. (In the general case $\boldsymbol{\Omega_{AB}}$ depends on the concentration of components and ***temperature.*** In those cases where $\boldsymbol{\Omega_{AB}}$ practically constant magnitude of $\boldsymbol{\Delta H_{shift}}$ of solution depends on the concentration of X_A and X_B).

In turn, the interaction parameter is equal to:

$$\Omega = ZN_{AB}[H_{AB} - (H_{AA} + H_{BB})/2] \tag{3.30}$$

where ***Z*** – average coordination number in the solution, $\boldsymbol{H_{AB}}$, $\boldsymbol{H_{AA}}$ and $\boldsymbol{H_{BB}}$ – ***A−B, A−A*** and ***B−B*** enthalpy bondings.

Task. Determine the average coordination number -Z for two-component solution consisting of 40% of component *A* and 60% of the component − B, if the valence of component *A* is equal to 3, and component *B* – 2.

Depending on the structure and size of thermodynamic functions of shifting, as well as the coefficient of activity γ may be highlighted number of solutions types. Let us dwell on the consideration of only two types of solutions: *ideal* and *regular.* The approximation of these types of solutions can be described by many metal and semiconductor solutions, both in solid and in liquid state. However, it should take into account the limitations of the ideal models and regular solutions in the first place because they take into account only the interaction between nearest neighbors. In Table 3.4. shown thermodynamic characteristics of the ideal and regular solutions. From the value of these characteristics should be the definition of these types of solutions.

In general case, $\Delta G_{см}$, **Δ*H***$\mathbf{\Delta H_{shift}}$, $\mathbf{\Delta S_{shift}}$, $\Delta V_{см}$ –consider the interaction between atoms in the solution.

Table 3.4. Thermodynamic characteristics of solutions

Thermodynamic characteristic	The value of thermodynamic characteristic for:	
	Ideal solution	regular solution
ΔV_{shift}	0	$\neq 0$
ΔH_{shift}	0 (Ω=0)	$X_A X_B \Omega_{AB}$
ΔS_{shift}	$- R (X_A \ln X_A - X_B \ln X_B)$	$- R (X_A \ln X_A - X_B \ln X_B)$
ΔG_{shift}	$RT (X_A \ln X_A - X_B \ln X_B)$	$X_A X_B \Omega_{AB} + RT (X_A \ln X_A + X_B \ln X_B)$
a_A *(concentration)*	X_A	$X_A \exp [\Omega_{AB}(1- X_A)^2/(RT)]$
a_B *(concentration)*	X_B	$X_B \exp [\Omega_{AB}(1- X_B)^2/(RT)]$
γ_A *(coefficient of activity A)*	1	$\exp \Omega_{AB}(1- X_A)^2/RT$
γ_B *(coefficient of activity B)*	1	$\exp \Omega_{AB}(1- X_B)^2/RT$

For **ideal solution** (mechanical mixture, there is no interaction between the components A and B) $\Delta V_{см} = 0$, $\Delta H_{shift} = 0$, H^0 and V^0 are additive that is determined by simple addition of the component; for the **regular solution** (B soluble in A, there is interaction A with B, and $\Omega \neq 0$) $\Delta V_{см} \neq 0$, $\Delta H_{shift} \neq 0$ H^0 and V^0 are not additive (enthalpy changing, shifting different kinds of atoms).

From thermodynamics follows that the formation of ideal solution under standard conditions is accompanied by changing in the isobaric-isothermal potential of shifting:

$$\Delta G_{см} = RT\ (X_A \ln X_A + X_B \ln X_B) \quad (3.31)$$

where – X_A and X_B – concentration of components – ***A*** and ***B*** in solution.

In the case of equilibrium coexistence of two ideal solutions (liquid and solid), based on the reference standard state ($T_{mA} > T_{mB}$) changing of ΔG_{shift} separately for each of the solutions of the form:

$$\Delta G_{см}^{Li} = X_A^{Li} \Delta G_{mA} + RT\,(X_A^{Li} \ln X_A^{Li} + X_B^{Li} \ln X_B^{Li}) \quad (3.32)$$

$$\Delta G_{см}^{So} = -X_A^{So} \Delta G_{mB} + RT\,(X_A^{So} \ln X_A^{So} + X_B^{So} \ln X_B^{So}) \quad (3.33)$$

At the same time it is known that during the phase transition

$$\Delta G = \Delta H - T\Delta S \quad (3.34)$$

For pure component at its melting point (T=T$_m$) thermodynamic potentials of the liquid and solid phases are equal to:

$$\Delta G_{mA}^{T=TmA} = (H_{Li} - H_{So}) - T_m(S_{Li} - S_{So}) = \Delta H_m - T_m \Delta S_m = 0$$

From which for pure component

$$\Delta H_m = T_m \Delta S_m; \qquad \Delta S_m = \Delta H_m / T_m.$$

At temperature different from T$_m$,

$$\Delta G_{mA}^{T \neq TmA} = \Delta H_m - T_m \Delta S_m \neq 0.$$

Given the dependence of $\Delta H_m = T_m \Delta S_m$ and neglecting small temperature dependence ΔH_m and ΔS_m the replacement ratio $\Delta H_m / T_m$, is obtained for each of the components at T ≠ T$_m$, respectively:

$$\Delta G_{mA} = \Delta H_{mA}(1 - T / T_{mA}); \quad (3.35)$$

$$\Delta G_{mB} = \Delta H_{mB}(1 - T / T_{mB}). \tag{3.36}$$

At equilibrium (coexistence) of the liquid and solid phase chemical potential μ for each component is the same both in liquid and in solid solution:

$$\mu_A^{So} = \mu_A^{Li}$$

$$\mu_B^{So} = \mu_B^{Li}$$

i.e. following relations is rightly:

$$d\Delta G_{см}^{So} / dX_A^{So} = d\Delta G_{см}^{Li} / dX_A^{Li}$$

$$d\Delta G_{см}^{So} / dX_B^{So} = d\Delta G_{см}^{Li} / dX_B^{Li}$$

Carry out further calculations relatively to the component *B*. Differentiating equations (3.32) and (3.33) and taking into account that $X_A = 1 - X_B$, we get, respectively:

$$\frac{\Delta G_{см}^{Li}}{dX_B} = -\Delta G_{mA} + RT(-\ln X_A^{Li} + \ln X_B^{Li}); \tag{3.37}$$

$$\frac{\Delta G_{So}}{dX_B} = -\Delta G_{mB} + RT(\ln X_B^{So} - \ln X_A^{So}); \tag{3.38}$$

Replacing ΔG_{mA} and ΔG_{mB} by their values from (3.35) and (3.36) and equating the right side to (3.37) and (3.38), we obtain:

$$-\ln\frac{X_B^{T\,So}}{X_B^{Li}} + \ln\frac{X_A^{So}}{X_A^{Li}} = \frac{\Delta H_{mA}}{R}\left(\frac{1}{T} - \frac{1}{T_{mA}}\right) - \frac{\Delta H_{mB}}{R}\left(\frac{1}{T} - \frac{1}{T_{mB}}\right) \tag{3.39}$$

Consider alloys near pure component *A*, i.e.

$X_A^{So} \to 1,\ X_A^{Li} \to 1,$ a $1/T \to 1/T_{mA}$,
under such conditions the value

$$\ln\frac{X_A^{So}}{X_A^{Li}} \to 0 \text{ and } \frac{\Delta H_{mA}}{R}\left(\frac{1}{T}-\frac{1}{T_{mA}}\right) \to 0$$

Hence, we obtain

$$\ln\frac{X_B^{So}}{X_B^{Li}} = \frac{\Delta H_{mB}}{R}\left(\frac{1}{T}-\frac{1}{T_{mB}}\right) \tag{3.40}$$

Repeating similar arguments for the diagram region near to component B, we get

$$\ln\frac{X_A^{So}}{X_A^{Li}} = \frac{\Delta H_{mA}}{R}\left(\frac{1}{T}-\frac{1}{T_{mA}}\right) \tag{3.41}$$

The equation of liquidus line for equilibrium with α-solid solution at low concentrations of component *B*, i.e. at $X_A^{So} \to 1$ has form

$$\ln X_A^{Li} = \ln\left(1 - X_B^{Li}\right) = \frac{\Delta H_{mA}}{R}\left(\frac{1}{T_{mA}}-\frac{1}{T}\right) \tag{3.42}$$

In the case of the formation of regular liquid solutions, equation (3.42) is transformed into

$$\ln a_A^{Li} = \frac{\Delta H_{mA}}{R}\left(\frac{1}{T_{mA}}-\frac{1}{T}\right) \tag{3.43}$$

The calculation of liquidus and solidus lines in the Ge-Si system, conducted with the help of expressions (3.40) and (3.41), gives good agreement between the calculated and experimental data. This indirectly proves that germanium and silicon is formed between each other practically close to ideal liquid and solid solutions.

In other cases, no such correspondence. The farther from the ideal solution, the greater the difference between calculated and experimental data. Thus, expression (3.40) and (3.41) can be used only in first approximation, in systems with unlimited solubility of components.

If liquid solution is ideal, and solid solution is regular (i.e. enthalpy change in the case of different kinds of atoms shifting in the solid solution $\Delta H_{см}^{So} \neq 0$), the expressions (3.40) and (3.41) are converted to the form:

$$\ln \frac{X_B^{So}}{X_B^{Li}} = \frac{\Delta H_{mB}}{RT} - \frac{\Delta S_{mB}}{R} - \frac{\Omega_{AB}^{So}\left(1 - X_B^{So}\right)^2}{RT} \tag{3.44}$$

$$\text{Or}\quad \ln \frac{X_A^{So}}{X_A^{Li}} = \frac{\Delta H_{mA}}{RT} - \frac{\Delta S_{mA}}{R} - \frac{\Omega_{AB}^{So}\left(1 - X_A^{So}\right)^2}{RT} \tag{3.45}$$

In the most general form of solutions for regular expressions (3.44) and (3.45) is converted into the equation of the form:

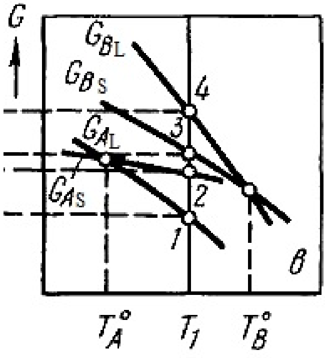
$$\ln \frac{X_i^{So}}{X_i^{li}} = \frac{\Delta H_{mi}}{RT} - \frac{\Delta S_{mi}}{R} - \frac{\Omega_{AB}^{So}\left(1 - X_i^{So}\right)^2}{RT} + \frac{\Omega_{AB}^{Li}\left(1 - X_i^{Li}\right)^2}{RT} \tag{3.46}$$

where ΔH_{mi} and ΔS_{mi} – entropy and enthalpy of component melting, ratio of the concentrations in the solid and liquid phases considered in the left side of the equation; X_i^{Li} and X_i^{So} – the concentration of i – component in the liquid and solid phases, respectively.

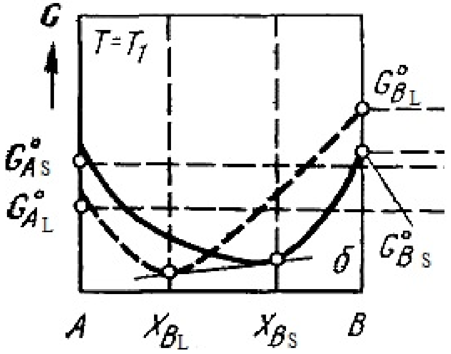
However, using equation (3.46) for the construction of the solidus and liquidus lines is not always possible due to lack of the thermodynamic characteristics of the solutions and their temperature and concentration dependence. They are usually only known for limited number of systems. Therefore, most often the problem is solved in the reverse order: the experimental phase diagrams build on the status of the liquidus and solidus lines in these diagrams determine the thermodynamic characteristics of the system.

Building EPD with unlimited solubility according to the change of the thermodynamic potential. To construct the equilibrium phase diagrams of binary systems, in which it is known that the interaction of the components leads to the formation of continuous series of solid and liquid solutions, and are known melting temperature of the pure components (T_A^o and T_B^o) and their temperature dependence G (T) are fed as follows:

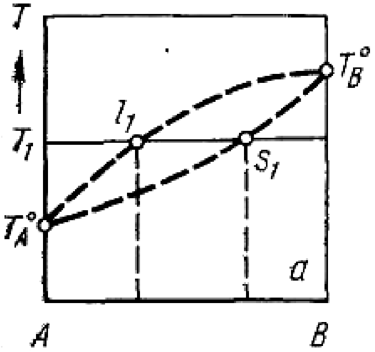
1) for several temperatures lying in the range between the melting temperatures of components (T_A^o < T_i < T_B^o), construct isothermal curves showing concentration dependence of the isobaric-isothermal potential of solid and liquid phases (Fig. 3.6. *a, б*);



a) temperature dependence G for A and B pure components in solid and liquid states,
T_A^0, T_B^0 – melting temperatures of A and B components



б) dependence of G for liquid and solid phases of variable composition at constant temperature T_1 (X_{Bl} and X_{Bs} –composition of liquid and solid phases in equilibrium at $T=T_1$)



в) solidus and liquidus curves

Figure 3.6. – Scheme of building solidus and liquidus curves from data on the temperature dependence G of pure A and B components in the solid and liquid phase (a), concentration dependence G of the solid and liquid phases in the case of binary system with unlimited solubility of the components in the solid and liquid states (a); *б*) the temperature dependence G of the pure A and B components in the solid and liquid states (X_B^{li} and X_B^{So} – composition of liquid and solid phases, which are in equilibrium at T_1)

2) through the graphical differentiation of these curves find coordinates of figurative points lying at selected temperature at the liquidus and solidus curves, corresponding to the compositions of the liquid and solid phases in equilibrium. The coordinates of figurative points are based on the fact that the values of the chemical potentials of the components at these points are equal to: $\mu_S = \mu_L$; or

$$\mu_{so} = \frac{\partial G_{so}}{\partial X_{so}} \; ; \; \mu_{li} = \frac{\partial G_{li}}{\partial X_{li}}$$ (Fig. 3.6. *б*),

3) upon receipt figurative points build liquidus and solidus curves (Fig. 3.6. *в*).

4) find the points lying on the solidus and liquidus curves at $T=T_1$. Find these points for other temperatures.

Distribution coefficient. The ratio of X_i^{So}/X_i^{Li} in (3.45) and (3.46) expressions is an important characteristic of the equilibrium between solid and liquid phases (crystal – melt). This ratio of the concentration of the solute in the solid in the liquid phase at the same temperature, called **distribution coefficient:**

$$\boldsymbol{k_0} = \frac{x_i^{so}}{x_i^{li}}\text{, at constant temperature}$$

From the diagram of phase equilibrium can be found values of equilibrium distribution of coefficients. However, since the solidus and liquidus lines are generally curvilinear, distribution coefficient k_0 depends on the X_i concentration:

$\boldsymbol{k_0}$ =f (X$_i$)

For approximate estimating of values $\boldsymbol{k_0}$ liquidus and solidus lines usually replaced by tangent near the main component (solvent), as shown in Fig. 3.7. In this case, the value of $\boldsymbol{k_0}$ at low concentrations can be considered independent of the concentration of $\boldsymbol{k_0} \neq$ f (X$_i$).

As follows from Fig. 3.7., coefficient $k_0 > 1$ corresponds to the case when the impurity increases the melting temperature of the solvent. At $k_0 < 1$ melting temperature of the solvent decreases with impurities dissolved therein.

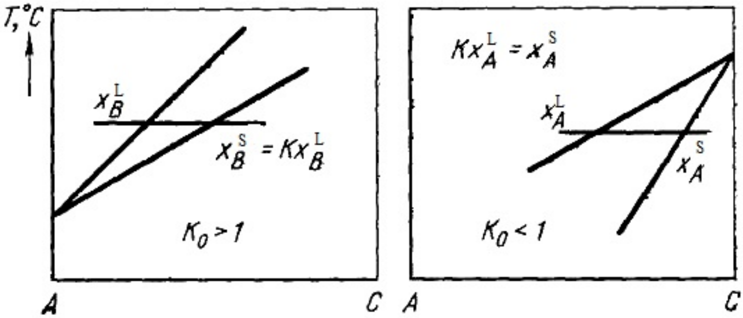


Figure 3.7. – Position of the liquidus and solidus lines near the component – solvent for cases $k_0 > 1$ and $k_0 < 1$.

Knowing the values of distribution coefficients is necessary to develop modes of metals and semiconductor materials treatment by zone melting: the more different from one k_0, the more effective the treatment.

From elementary diamond-like semiconductors (Ge, Si, C) diagram of phase equilibrium with unlimited solubility form only Ge and Si. They fully meet the above requirements.

Si and C (diamond) meet the requirements of the chemical bonding (nature) and the type of lattice, but differ greatly on the size of tetrahedral covalent radii:

$$R_{Si}=0{,}117 \text{ nm},\ R_c=0{,}077 \text{ nm},\ \frac{\Delta R}{R_{Si}} = 36\% \text{ » } (10\div15)\%$$

Therefore, the solubility of C in the Si is less than percent, and Si in C even less.

Unlimited solubility – is very common phenomena among semiconductor compounds. They form a lot of connections between classes: $A^{III}B^{V}$, $A^{II}B^{VI}$, $A^{IV}B^{VI}$, $A^{III}B^{V}$ $A^{V}B^{VI}$ and others.

Such solid solutions are widely used. This is facilitated by the fact that solid solutions of semiconductors with unlimited solubility allows to obtain alloys with any values of bandgap, lattice period (interatomic distances), coefficients of thermal expansion and number of other parameters. The lattice period, in first approximation changed additively (Vegard rule), other parameters – for more complex laws. Given the opportunities created by such solid solutions, establishing the dependence of their properties on the composition is important task of material science.

Tasks:

3.1. Determine the melting entropy of ΔS_m for Fe, W, Si, Te and compare obtained values with the character of changes in chemical bondings of these materials during the melting (melting temperature of Fe, W, Si and Te 1530, 3416, 1412, and 450 ^{o}C, respectively).

3.2. Ge contains the same concentration of background (harmful) impurity Cu ($k_{oCu} = 1{,}5\cdot10^{-5}$) and Sn ($k_{oSn} = 2\cdot10^{-2}$). Before obtaining from such material of perfect single crystal by the Czochralski method (from liquid solution-molten) it is subjected to zone melting for decreasing the concentration of Cu and Sn by several orders of magnitude. Which of impurities requires fewer passes of zone melting?

3.3. How to change the value of distribution coefficient of impurities (if $k_0 < 1$ and $k_0 > 1$) by increasing the rate of crystal growth due to increased supercooling of the melt.

3.4. Water (ice) is formed with unknown impurity solution with unlimited solubility of the components in the liquid and solid state. This impurity increases the melting point of ice. At certain temperature T system is in two-phase state ($S + L$). At one of the phases of the impurity concentration is less than at this T?

3.5. Water with impurity is carried on frost. Half of water froze. Where impurities will be more: in the unfrozen water or ice? Consider the task for two cases: 1) $k_0 > 1$ (impurity increases the temperature of melting ice); 2) $k_0 < 1$ (impurity decrases the melting temperature of ice).

§ 6. T – X – diagrams of phase equilibrium of binary systems with unlimited solubility of the components

Unlimited solubility of the components in each other is relatively rare, more often occur their interaction is complex.

Within one binary system in different ranges of concentration can be realized (and often realized) different phases, which leads to complication of the phase equilibrium diagrams.

Transition from unlimited solubility to limited. Thermodynamic analysis provides qualitative and in many cases quantitatively explain the transition from diagram with unlimited solubility to other types of phase diagrams. The starting point for deciding on the outcome of different kinds atoms interaction in their shifting is sign of the isobaric-isothermal potential of shifting:

$$\Delta G_{см} = \Delta H_{см} - T\Delta S_{см}$$

The amount of $\Delta G_{см}$ difficult depends on several factors, the main ones are two:

1) chemical, taking into account the degree of chemical affinity of the components (their valence, electronegativity, lattice type);

2) geometrical, taking into account the difference in the "atomic sizes" interacting components during the formation of solution: where $\Delta R = (R_A - R_B)/R_A$ - the atomic radii of *A* and *B* components, defined by chemical bonding occurring during the formation of solution.

Increasing of components chemical affinity reduces the internal energy of the phase U, and therefore enthalpy value, as

$$H = U + PV = U_0 + U_T + U_E + PV \tag{3.47}$$

however in this case $\Delta H_{см}$ must be negative.

Increasing the difference in the sizes of interacting atoms $|\Delta R|$ should cause increasing in the internal energy U and enthalpy H, respectively, including the case of solid solution by increasing elastic deformation energy of the lattice (U_E); thus it must be positive.

It is necessary to distinguish the cases of chemical interaction in the formation of solid solution between nearest-neighbor atoms of one species (*A–A*) or (*B–B*) and the interaction between nearest-neighbor atoms of different types (*A–B*). The corresponding binding (enthalpy) energy and denoted by H_{AA}, H_{BB} and H_{AB}.

In the case of ideal solution binding energy of atoms pairs of different kinds will be equal to the average of binding energy of the pairs of atoms of one kind, that is

$$H_{AB} = 1/2(H_{AA} + H_{BB}) \tag{3.48}$$

In this case, the enthalpy of shifting $\Delta H_{см} = 0$, as well as the interaction parameter $\Omega = 0$ (see. Table. 3.4).

In the real solution $\Delta H_{см} \neq 0$. The sign of the enthalpy of shifting depends on the sign of Ω. Size of $\Delta H_{см}$, can be negative or positive.

It should, however, take into account that the result of components interaction is determined by value $\Delta H_{см}$ only at low temperatures: T→0. With increasing temperature, according to the expression (3.27) becomes significant part of $T\Delta S_{см}$ derivative (the so-called entropy term).

Diagrams of phase equilibria with eutectic transition. In binary systems, in which the *crystalline structure of the components are different, and their dissolution in each other leading to decreasing of crystallization temperature,* can occur eutectic[*] transformation.

Diagram with eutectic is shown schematically in Fig. 3.8*a*. It consists of six phase regions: single-phase region of liquid solution *L,* two-phase regions liquid solution *L*+ α solid solution and liquid solution *L*+ β solid solution; single-phase regions of α and β primary solid solutions; two-phase region of coexistence of α + β solid solutions.

Slope of *A'e* and *B'e* liquidus line represent the geometrical place of figurative points of liquid solutions with limit concentration at appropriate temperatures.

Slope of *A'c* and *B'd* solidus line is the geometrical place of figurative points of solid solutions with limit concentration that exist in certain temperatures above the eutectic temperature T_e.

The horizontal line *ced*- is a eutectic line. Only three points on the *ced* line are figurative, they characterize limiting concentration of solid solutions α (point *c*) and β (point *d*) and the liquid solution (point e) at temperature of eutectic transformation.

[*] *eutectic (eutektos – (greek) – easily meltable) – fine solids mixture simultaneously crystallize from the melt at temperature lower than the melting temperature of the individual components.*

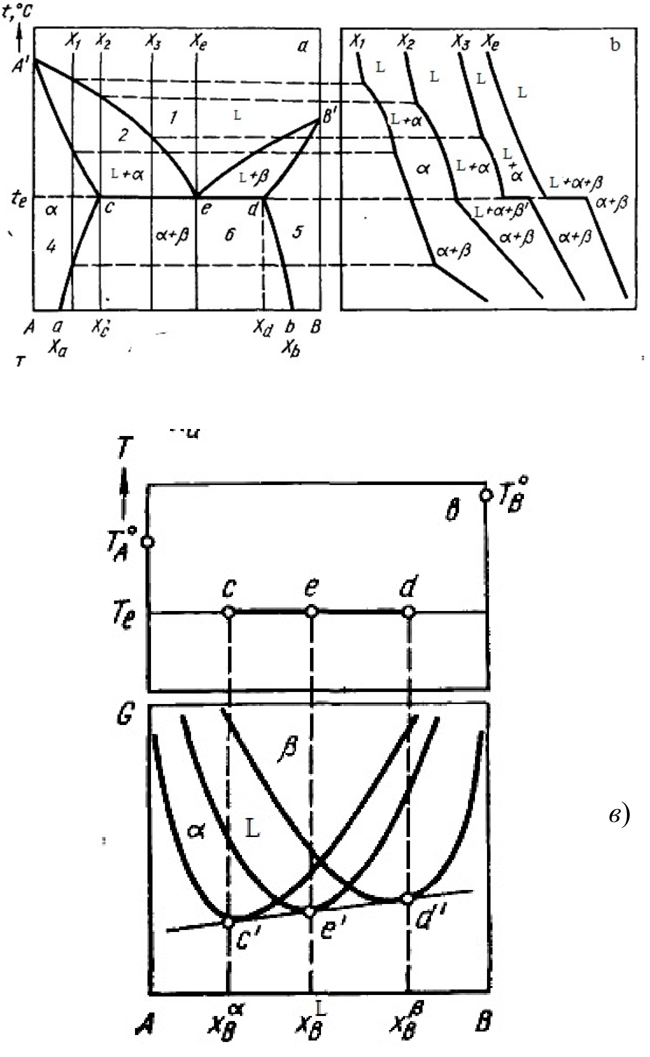


Figure 3.8. – Phase diagram of binary system with eutectic break of solubility: *a* –phase equilibria; *б* – cooling curve of alloys shown in the diagram; *в* –- isobaric-isothermal potentials curves of liquid and solid phases at the eutectic temperature T_e:

$$\left(\frac{\partial G^{\alpha}}{\partial X_B^{\alpha}}\right)_{c'} = \left(\frac{\partial G^{Li}}{\partial X_B^{Li}}\right)_{e_1'} \cdot \left(\frac{\partial G^{\beta}}{\partial X_B^{\beta}}\right)_{d'}.$$

In Fig. 3.8*в* given the structure of isobaric-isothermal potentials curves of solid solutions α and β, and the liquid solution at the eutectic temperature. The eutectic temperature T_e and the position of eutectic points (*e* points) in the case of formation in the system of ideal liquid solutions and low solubility of the components in one another in the solid state can be calculated from the joint solution of the equations of liquidus components *A* and *B*:

$$\begin{aligned} &\exp\left[\frac{\Delta H_A}{R}\left(\frac{1}{T_A}-\frac{1}{T_E}\right)\right]+\exp\left[\frac{\Delta H_B}{R}\left(\frac{1}{T_B}-\frac{1}{T_E}\right)\right]=1; \\ &X_A+X_B=1. \end{aligned} \tag{3.49}$$

Feature of *ced* eutectic line consists in that at the eutectic temperature (T_e) in the composition of alloys from *c* to *d* in equilibrium are three phase of the above composition.

Task. Determine the number of freedom degrees *C* in the alloys from *c* to *d* at T_e.

ac and *bd* sloping lines – geometric places of figurative points of limit concentration of solid solutions that exist at temperatures below the eutectic (solubility curves).

During cooling of the single-phase region at line of intersection with the oblique line structure diagram of the alloy is in state saturated with the solution. Below the point of intersection begins disintegration of the supersaturated solution with the release of another phase, composition of which characterizes the point of intersection of conodes with the second oblique line bounding this two-phase region. Upon cooling within the two-phase region while changing the composition of two phases and their relative proportions.

The compositions of alloys from *c* to *d* occurs decay of liquid solution of the composition *e* to two solid solutions *c* and *d* cooling by the reaction:

$$L_e \leftrightarrow S_c + S_d \text{ (cooling} \leftrightarrow \text{heating)} \tag{3.50}$$

In the diagram in Fig. 3.8*a* shows the characteristic line of four alloys and corresponding cooling curves indicating the phase composition of alloys in different temperature ranges. The length of region on the cooling curve associated with invariant transformation of alloys X_3 and X_e, is proportional to the amount of liquid melt, turning into eutectic mixture at temperature T_e. For alloy X_e this amount is 100%, and for alloys X_1 and X_2 is 0% for others determined by the lever rule or law of additivity[1].

Note that when cooling any alloy, lying in the two-phase region α+β, starting from the temperature T_e, changing the composition of both the solid solution on the curves *ca* and *db* (thus they are depleted by dissolved component) and the quantitative ratio of the phases is determined according to the rule lever.

For diagrams with eutectic is necessary to introduce, in addition to the concept of "phase", even the concept of "structural component". For diagram with unlimited solubility of these concepts are the same.

In the α + β phase diagram with eutectic alloy phase composition for any alloy is the same – it is a mixture of phases α and β, but in terms of formation these phases, alloy differ by the nature of their location and form of particles. This distinction is important because the properties of alloys are dependent not only on the composition of phases but also on the geometry and nature of the particulate phase components of interposition.

The structural components are primary crystals are released from the supersaturated liquid melt along the inclined lines (solidus) of diagrams; secondary crystals were released from the supersaturated solid solution along the inclined lines (lines of solubility) of the

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[1] Quantification comparison of the size of horizontal regions on curves of cooling or heating is possible only for alloys of identical mass.

diagram; eutectic (eutectic mixture), representing mixture of the crystals of two solid phases are simultaneously formed by the eutectic reaction (3.50). Schematic view of the various structural components[2] shown in Fig. 3.9.

Thus, alloys in the system shown in Fig. 3.8 *a*, comprise the following constituents:

from A to X_α – α- primary crystals;

from X_α to X_c – α- primary + β- secondary crystals;

from X_c to X_e (hypoeutectic alloys) – α- primary crystals + eutectic (α + β)+ β- secondary crystals;

X_e (eutectic alloy) – eutectic (α+β);

from X_e to X_d (hypereutectic alloys) – β- primary crystals + eutectic (α+β) + α- secondary crystals;

from X_d to X_b – β- primary + α- secondary crystals;

from X_b to B – β- primary crystals.

Diagrams with eutectic schematically described above are characterized by the fact that the maximum concentration of solutions α and β relatively large. Mutual solubility of the components, although limited, but is few to tens of percent. In these cases, the two components are elements with the same nature of chemical bondings.

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[2] When at eutectic transition temperature eutectic consists of primary crystals and in the case of decreasing temperature, appears the secondary crystals in it.

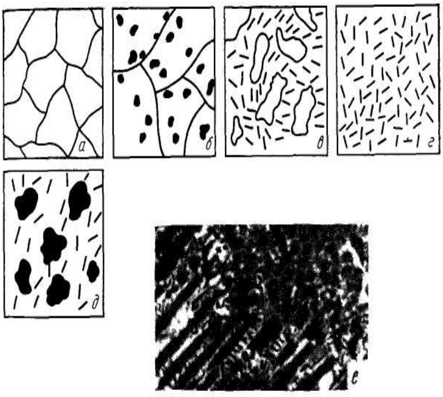


Figure 3.9. – Schematic image of some alloys structure of diagram with eutectic break solubility containing different structural components (*а*-*д*) and structure of the eutectic alloy quasibinary system of InTe-Sb_2 (*е*) [alloy composition of 72% (mol.) Sb_2 – 28% (mol). InTe; ×120]; and *а* – α-primary crystals; *б* – α-primary crystals + β-secondary crystals; *в* –α-primary «eutectic» (α + β); *г* –«eutectic» (α+β); *д* – β-primary crystal + eutectic.

Diagrams of phase equilibrium with degenerate eutectic transition. If one of the components of binary system semiconductor, i.e. has directed and saturated bondings and therefore poorly soluble in elements of different nature of bondings (great $\Delta H_{см}$), phase diagram changes. Metal-semiconductor phase diagrams are schematically shown in Fig. 3.10.

Diagrams of the type shown in Fig. 3.10*a,* characteristic for systems Ag-Ge, Au-Ge, Al-Si. Diagrams of the type shown in Fig. 3. 10*б*, which called as diagram with degenerate eutectic (eutectic point close to the pure components) characterize the equilibrium in systems of In-Ge, Pb-Ge, Ga-Si, Zn-Si, Tl-Ge, Bi-Ge, Sn-Ge.

Investigations carried out with the use of ultra-pure materials, the latest high-precision methods of structural analysis and measurement of electro-physical parameters have shown that there is always at least negligible mutual solubility of components. This confirms the validity of thermodynamic output, said earlier. Metals are dissolved in semiconductors, but in very small quantities that are calculated in hundredths and thousandths of atomic percent.

To display such low solubility in the phase diagrams is used, as mentioned above, the introduction of scale on the concentration axis. As an example is used phase diagrams image of Fe-Si and Si-Au (in Fig. 3.1).

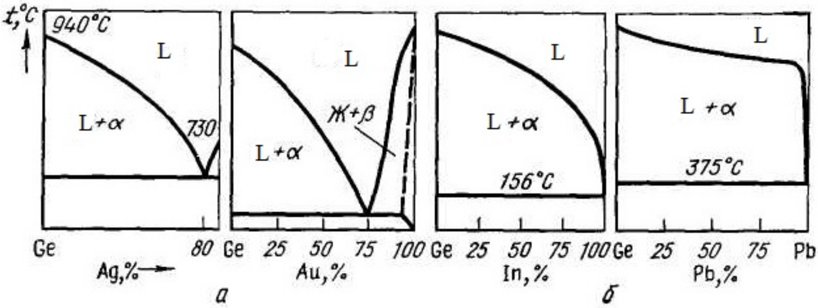


Figure 3.10. Phase diagrams of semiconductor-metal system with normal (*a*) and degenerate (*б*) eutectic.

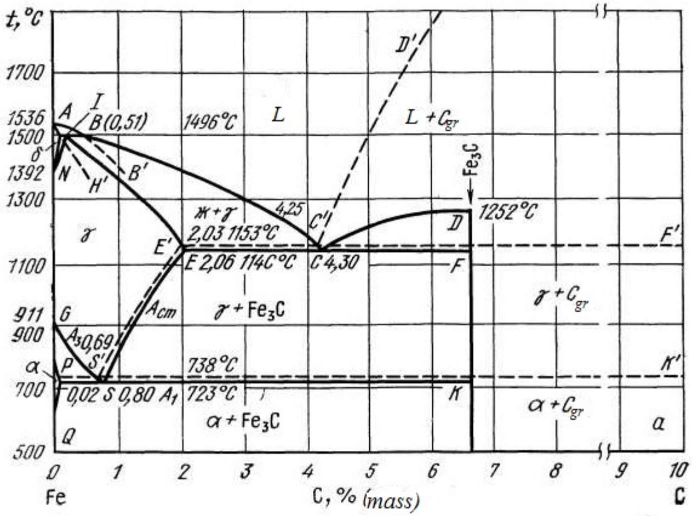
The solubility of metals in semiconductors was not only small, but also dependent to temperature, which have great practical importance. As previously reviewed diagrams with eutectic maximum solubility of one component in the other occurred at the eutectic temperature T_e. This regularity holds for most metal-based solutions. However, in the case of solutions based on semiconductors (Ge, Si, $A^{III}B^{V}$ type compound) the maximum solubility is observed at temperatures well above the eutectic, and decreases towards the eutectic temperature T_e in several times. Thus, in the Si-Au and Si-Fe systems (see. Fig. 3.1) solubility at T_e in 10 – 15 times lower than the maximum temperature (at $T > T_e$). This kind of dissolution, when it corresponds to the temperature exceeding the eutectic, called as ***retrograde solubility.*** Retrograde solubility is observed, for example, for solid solutions of metal in Ge, Si and $A^{III}B^{V}$ semiconductors. In solid solutions of metal-based retrograde solubility is rare. Thermodynamic causes of retrograde solubility insufficiently studied. It is related to the large value of the shifting enthalpy by dissolving impurities in semiconductors.

Diagrams of phase equilibria with the eutectoid transformation.

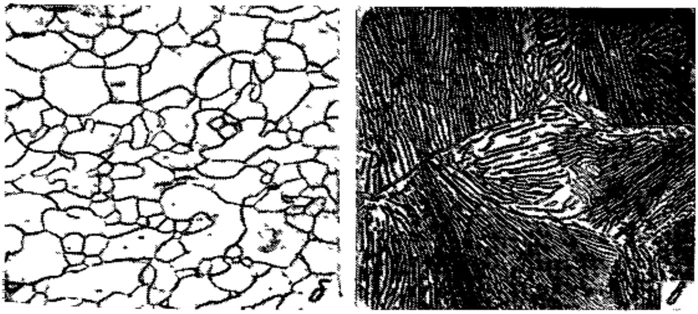
Transformations of eutectic type may experience not only liquid but also solid solutions. Non-variant transformation consists in the decomposition of the solid solution into two other solid phase, called the eutectoid, and the corresponding structural component – eutectoid.

$$S_1 \leftrightarrow S_2 + S_3,\ \text{(cooling} \leftrightarrow \text{heating)} \qquad (3.51)$$

A typical example of eutectoid transformation can serve transformation in the Fe-C system (Fig. 3.11).



a



б *в*

Figure 3.11. The phase diagram of Fe-C system (*a*) and typical structure of the alloys of this system (*б, в*) after slow cooling (*б* – ferrite with carbon content of 0.6% (*в* – eutectoid steel).

In this system, austenite (solid solution of carbon in γ-iron with FCC lattice) containing 0.8% C, decomposes at 723 °C in mixture of two phases: Fe_3C iron carbide (cementite) and solid solution of carbon in α-iron (BCC lattice) containing 0.04% C (ferrite):

$$\gamma \leftrightarrow \alpha + Fe_3C, \ \text{(cooling} \leftrightarrow \text{heating)}$$

Task. Determine the number of freedom degrees *C* at peretectoid transformation.

Eutectoid structural component, comprising last two phases, called perlite. Number of perlite, shape and size of its constituent cementite particles have decisive effect on the properties of steel.

This example well illustrates another important feature of the eutectoid transformation: it is associated with the movement (diffusion) of the components in solid solution at very long distance. Thus, to steel containing 0.8% C at eutectoid transformation produced Fe_3C particles with the size of hundredth of micrometer (100 nm), carbon atoms have to collect from the 1.5 million unit cells.

Character of diagrams with eutectic in semiconductor – metal systems plays an important role in the selection of alloys for doping of semiconductors and formation of contacts by fusing or melting – diffusion methods.

Diagrams of phase equilibria with peritectic transformation. One feature of the above diagrams with eutectic is that *A* and *B* components, dissolved in one another, decreasing melting temperature of solution both from *A* and from *B*.

If, however, at limited solubility of components in each other one of them, for example *B*, dissolving in *A,* decreasing melting temperature of solutions based on it, as component *A,* dissolving in *B,* on the contrary, increases the T_m of solution instead of eutectic transition in diagram present as called ***peritectic*** transformation (*n* – peritectic point of transformation, Fig. 3.12 *a*).

Eutectic transformation in binary system is the solution decay while cooling on the other two phases; peritectic transformation, on the contrary, is process of forming single phase through the interaction of the two other phases, completely or partially disappears at this. This reaction is written as follows: (cooling ↔ heating)

$$L + S_{b1} \leftrightarrow S_{b2} \quad \text{or} \quad L + \alpha \leftrightarrow \beta \qquad (3.52)$$

Peritectic transformation in binary system is non-variant. Compositions of three equilibrium phases, as in the eutectic line, determined by the intersection points of *ab* horizontal line of peritectic with slanted lines in the phase diagram (i.e. *a*, *n*, *b* points)

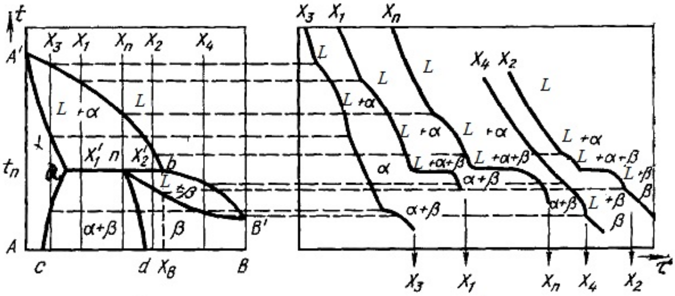


Figure 3.12.

In Figure 3.12. *б* shown the cooling curves for the five alloys like X_n, X_1, X_2, X_3, X_4, compositions of which are shown in Fig. 3.12 *a.* On cooling curves indicated phase composition of the alloys in different temperature ranges.

Task. To determine the variance of the system at temperature T_n, Fig. 3.12 *a*.

The length of region on the cooling curves at T_n for X_n, X_1, X_2 alloys is proportional to the number[3] of interacting liquid solution and solid phase (by phase number formed by the peritectic reduction at T_n). For X_n alloy these relative amounts to 100%, for the other alloys of the region extent using the right lever can determine the proportion of alloy undergoes peritectic transformation.

For alloys which compositions lie in the range of from X_a to X_n, the amount of liquid phase at temperature T_n is not enough for occurring interaction with all solid phase. As result, after peritectic transformation besides the new phase, alloys will contain an excess amount of primary crystals of α phase. For X_1 alloy at temperature just below T_n excess amount of crystals in the alloy equal to $(X_{1n}/an)\cdot100\%$.

Similarly, for the alloys which compositions lie in the range of from X_n to X_b, the number of phases α at T_n is small compared with the amount of liquid phase. As result, upon completion of peritectic conversion in alloys remain excess amount of the liquid phase.

In X_2 alloy its relative amount is $(nX_2/nb_L)\cdot100\%$.

An important feature of peritectic systems is that when the crystallization temperature T_n is completed only part of alloy undergoing peritectic transformation. As can be seen from the diagram in Fig. 3.12 alloys in the range of from X_n to X crystallization completed below T_n in line *nB*'.

Liquidus line (beginning of crystallization) is the line *A*'*bB*', and the solidus line – the line *A*'*anB*'. Line *aC* is called the solubility curve. Line *ab* – peritectic horizontal, in which lies *a*, *n* and *b* three figurative points, corresponding to the composition of phases undergoing non-variant transformation.

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[3] Quantitative comparison of the sizes of horizontal regions on cooling or heating curves is possible only for alloys of identical mass.

If transformation similar to peritectic occurs only involving of solid phases, it is called ***peritectoid.***

$$S_1 + S_2 \leftrightarrow S_3 \quad \text{or} \quad \alpha + \beta \leftrightarrow \gamma \qquad (3.53)$$

(cooling ↔ heating)

Diagrams of phase equilibria with chemical compounds. As noted before, in case of large negative quantity of shifting heat $\left| -\Delta H_{см}^{so} \right|$, i.e. in the case of large chemical affinity of system components and their interaction leads to the formation of chemical compounds. On the phase equilibrium diagram of chemical compounds are represented by ***vertical lines*** (at high temperatures can be observed deviation from the vertical).

Consider the features of the phase diagrams with chemical compounds. From this perspective, all compounds can be classified in two ways:

1) by the ratio of the compounds and liquid phase formed during the melting of this compound. Compounds for which these compositions are same, are called ***congruent melting*** or ***persistent***. If compositions are not identical, the compounds are called ***incongruently melting*** or ***unstable;***

2) ability to dissolve other components in itself, including components of the compound, or alternatively, the ability to form solid solutions on their basis.

One phase region of solid solutions of the components in this compound called homogeneity region.

There are compounds with wide range of homogeneity region, calculated in percents, and compounds with narrow homogeneity region, calculate decimals and less proportions of percents and are not detectable in the phase equilibrium diagram, constructed in the normal scale.

Congruently melting compounds are formed in many systems with semiconductor phases: A^{III}–B^{III}, A^{III}–B^{IV} and others. The melting temperature of such compounds lies on the liquidus line and line itself is a curve with maximum, which in many cases corresponds to the compound composition (Fig. 3.13 *a*). *(Congruence – latin, congruens (congruentis) proportionate, appropriate, matching; in geometry – proportionality, matching,* *match. Homogeneous – greek, homogenes – composition).* This system always contains normal or degenerate eutectic and can be divided into partial simple eutectic systems, where compounds act as components of these systems and, therefore, compound ordinate divided diagram for private diagrams: M = q+1, where M – number of partial diagrams, q – number of congruently melting compounds in the system. Thus, systems of In-As and Ga-As are divided into two simple eutectic, Gr-Si – to four, i.e. congruently melting compound acts as system component.

Incongruent melting compounds (Fig. 3.13). Melting of this type compounds, for example Ga_3Te_4 (Fig. 3.13. *a*), occur as peritectic type of transformation during heating, i.e. solid phase is converted into two phases – liquid and solid, the compositions of which lie on both sides of the composition of starting compound. Thus, ***the melting temperature of compound is below the liquidus line,*** whereby the latter ***does not have maximum*** associated with the compound.

If in the system in addition to incongruent melting, there is congruently melting compound, then in appropriate range of concentrations for the liquidus line will experience maximum, as in the case with Ga-Te (see. Fig. 3.13 *a*) in the case of compounds GaTe and Ga_2Te_3. Break state diagram with unstable compounds into simple diagrams, taking the compound as component of the system, it is impossible.

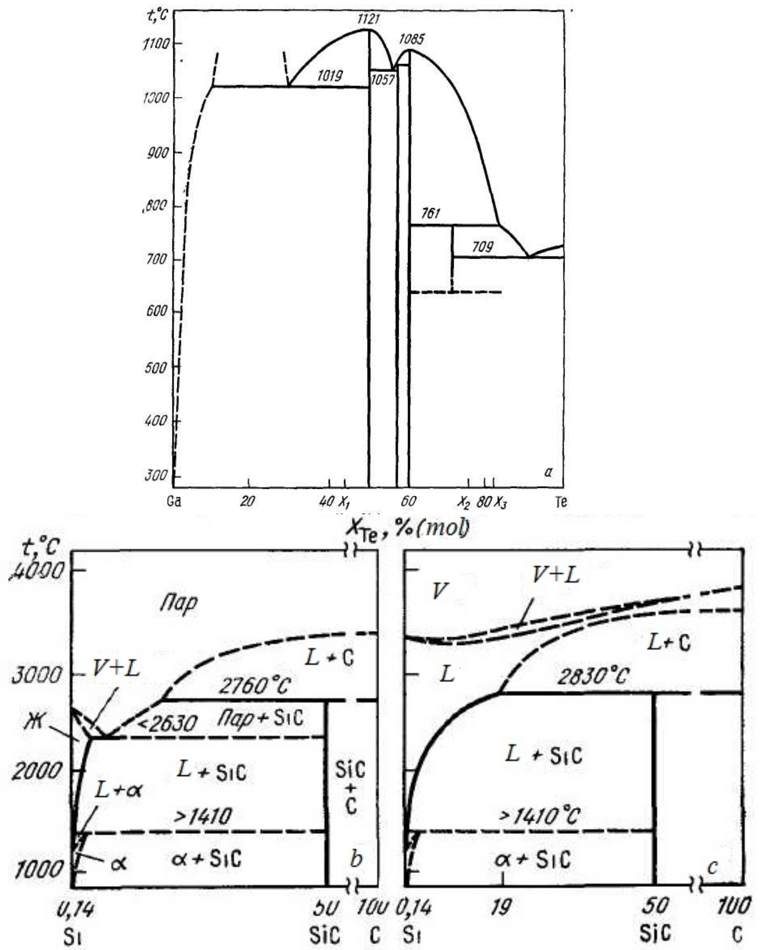

Figure 3.13. – Phase diagram of systems with stable and unstable chemical compounds: *a* – system of Ga-Te, which produces two stable (GaTe and Ga_2Te_3) and two unstable (Ga_3Te_4 and Ga_2Te_5) compounds; *б*, *в* – Si-C systems at pressure P ≈100 (*б*) и P~1 (*в*); in system formed stable compound of SiC. In the system of Ga-Te melting temperatures of 1121, 1057, 1085ºC corresponding to GaTe, Ga_3Te_4, Ga_2Te_3 compounds.

Compounds forming broad region of homogeneity. Compounds of this type are quite common in metal and semiconductor systems (metal compounds such as interstitial phases, chalcogenides, and others). Among the compounds of this type identified two groups: ***daltonides and berthollides***.

Daltonides – compounds with broad homogeneity region – characterized by the fact that the formulaic composition of compound within the homogeneity region (Fig. 3.14 *а*, *б*, *в*); common to the diagrams with daltonide phases is the presence of singular point on the liquidus and solidus curves, the composition of which corresponds to daltonides and simple stoichiometric ratio of the components. In the diagram of structure – property to formulaic composition of compound corresponds extreme value of properties.

Berthollides characterized by the fact that formulaic composition of the compound lies outside of homogeneity region (see. Fig. 3.14 *г*, *д*). This means that for compounds of bertollide type of formulaic composition does not exist. The alloy corresponding to the formula of compound consisted of two phases, one of which is solid solution based on compound. Isochoric-isothermal potential of such two-phase mixture is less than isochoric-isothermal potential of compound strictly formulaic composition. In structure – properties diagram within the compositions of the homogeneity region, properties change monotonically.

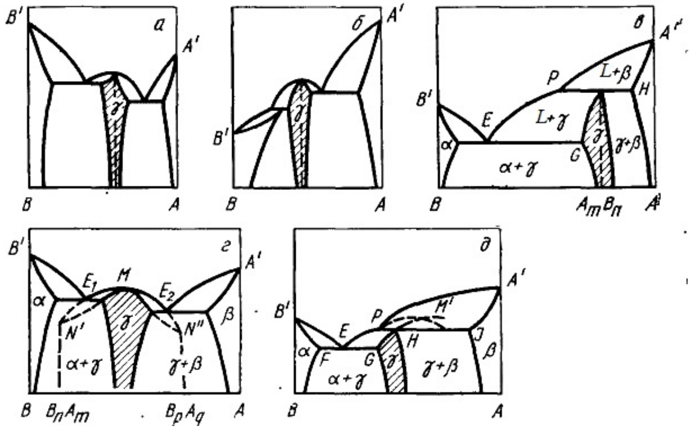

Figure 3.14. – Systems that are formed daltonide (*а*, *б*, *в*) and bertolide (*г*, *д*)

phases; *а, б* – A_xB_y and A_kB_p compounds are congruent melting daltonide phases; *в* – incongruent melting A_mB_n compound – daltonide phase; *г* – γ phase with open maximum (liquidus curve) – bertollide phase; *д* – γ phase with concealed maximum (liquidus curve) – bertollide phase. In Fig. *а* shaded region of homogeneity of A_xB_y compound, in Fig. *б* – A_kB_p compound.

Compounds which form the narrow region of homogeneity. These include the majority of semiconductor compounds which form narrow range of solid solutions with components in the composition of compounds. Thus, the region width ranges from ten (for example, in compounds of $A_2^{III}B_3^{VI}$ type, so much for In_2Te_3 from 59.5 to 60% Te) to hundredths ($A^{II}B^{VI}$) and even to thousandths ($A^{III}B^{V}$) of atomic percent. Despite the small amount, solubility plays a critical role in formation of compound physical properties. Therefore, study of features of solid solutions arranged in narrow region of homogeneity (i.e. with an excess of *A* and *B* components), is important and experimentally difficult task.

One of the features is that in very large number of cases on the basis of $A^{III}B^{V}$ and $A^{II}B^{VI}$ compounds within the homogeneity region formed superposition of solid solutions, for example omission solid solution and interstitial solid solution. The second feature is that the maximum melting temperature is necessary in these cases, the compositions are somewhat different from the stoichiometric compound and get strictly stoichiometric composition is difficult. Such compounds are called compounds with shifted *stoichiometry*. However, during small deviation from the stoichiometric composition, the compound melts with open maximum, are considered (in first approximation) as congruently melting compound.

§ 7. Dual semiconductor and dielectric phases

General classification of dual semiconductor compounds did not exist. The most rational classification is based on the union to one class of compounds having the same stoichiometric formula and formed from the elements arranged in same groups of the periodic table of elements. Elements located in the periodic table in subgroups with fewer sequence numbers are designated by the letter A, and in subgroups with larger sequence numbers marked b B. Designations of elements of $A^{III}B^{V}$ type should not be confused with their position in the periodic table, in the subgroups.

For example, compounds of class $A^{III}B^{V}$: GaAs. GaP, InSb formed by elements arranged in III A and V subgroups of the periodic system and its constituent compounds in equivalent proportions.

$A_2^V B_3^{VI}$: $B_2Te_{3,} Sb_2Te_{3,} As_2Se_3$ class of compounds formed by elements located in the V A and VI subgroups of the periodic system and includes in ratio of 2: 3.

Thus, class formula is generalized stoichiometric formula compounds included in this class.

Regularities of binary phase semiconductor formation. Double semiconductor phases are double semiconductor compounds and solid solutions based on them. Chemical bondings in these phases mixed with covalent component predominance. Most often it is covalently-ionic-metalic bonding. Less is covalently-ionic.

Ionic component of the bonding due to the fact that double phase constructed of dissimilar atoms. It characterizes the probability of belonging electrons to one of atoms, forming the bonding; if this probability is $\frac{1}{2}$, ionic component is equal to zero.

Metallic component characterizes the degree of blur cloud of valence electrons, forming chemical bonding.

In the case of elementary semiconductors generalized qualitative characteristic of chemical bonding in the subgroup is the serial number of element.

In the case of binary compounds generalized quantitative characteristic of chemical bonding in the same class of compounds is the average atomic number of compound:

$$Z_{cp} = \frac{\Sigma C_i Z_i}{\Sigma C_i} \tag{3 .54}$$

where C_i – number of atoms of i – component;

Z_i – serial number of i -component.

For example, Z_{cp} for GaAs is equal to 32: $Z_{cp\ GaAs} = (31+33)/2 = 32$; Z_{cp} of sesquioxide indium telluride (In_2Te_3) $Z_{cp\ In2Te3} = (2*49+3*52)/5 = 50{,}8$

Within the class of compounds there is correlation between the properties of compounds and their average atomic number.

Dual semiconductor phases are formed when essentially in hybrid bondings: sp, sp^2, sp^3, dsp, d^2sp^3 and others.

The presence of mixed bondings leads to complex crystal structure phase.

Description of formation structures by Pauling (1935 y). For description of some structures Pauling introduced the concept of chemical bondings resonance.

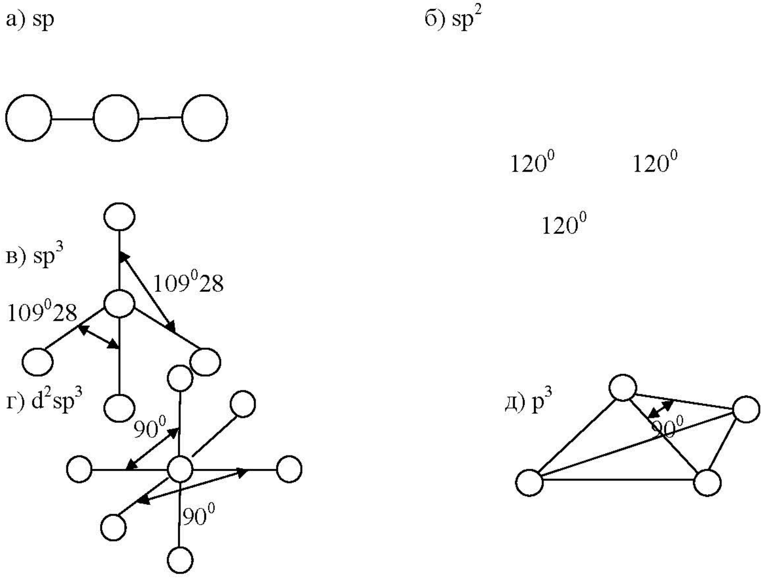

Figure 3.15. – Spatial configurations of bondings implemented by orbitals:
а) sp; – diagonal linear configuration, $Z_k=2$;
б) sp^2; – trigonal planar, $Z_k=3$;
в) sp^3; tetrahedral, $Z_k=4$;
г) $d^2 3p^3$ – octahedral, $Z_k = 6$;
д) trigonal pyramidal, $Z_k = 3$.

It was found that most of the studied binary semiconductor phase subject to the following empirical regularities:

1) In most dual semiconductor phases performed the relation of Mooseri-Pearson (Canadian scientists):

$$(n_e/n_a) + в = 8 \tag{3.55}$$

where n_e – number of valence electrons per formula of the compound (or the number of electrons participating in the formation of bondings);

n_a – number of element atoms- anion, IV – VII B subgroup element accounting for the formula of the compound;

в – average number of chemical bondings between atoms of element – anion per atom of the anion; determination of ***в*** value requires knowledge of the crystal structure of compound.

«–» anion (greek ana – up) – negatively charged ion;

«+» cation (greek кata – down) – positively charged ion.

Phase, for which Mooseri-Pearson rule is executed effectively completes the valence shell of element atom – anion to 8. Rule of Mooseri-Pearson is equivalent (octets) to the Hume-Rothery rule for elementary semiconductors.

Hume-Rothery first show that the structure of covalent crystals of chemical elements belonging to different groups of the periodic system and satisfies the rule:

$$Z_k = 8 - N \tag{3.56}$$

where Z_k – coordination number;

N – number of group in which located element (N – equal to the valence of the element);

Z_k is equal to the number of atom’s covalent bondings. Covalent crystal structure determined by the Hume-Rothery rule and direction of bondings, which can be found from the analysis of the wavefunctions of valence electrons. Covalent bondings as opposed to metallic characterized by orientation and saturation.

Hume-Rothery rule can be written as follows:

$$N_{в} + Z_k = 8 \qquad (3.57)$$

where $N_{в}$ – number of valence electrons of element (for elements subject to the Hume-Rothery rule, it coincide with the number of the periodic system);

Z_k – number of valence electrons "give" on the formation of the chemical bonding by atoms of the first coordination sphere. This entry Hume-Rothery rule emphasizes the role of short-range order in the formation of semiconductor structures. In Table 3.5 shown examples of calculations by Mooseri – Pearson rule.

Table 3.5. Examples of calculations according to the Mooseri – Pearson rule

Compound	Class	n_e	n_a	в	(n_e/n_a) +в
GaAs	$A^{III}B^{V}$	8	1	0	8
CdTe	$A^{II}B^{VI}$	8	1	0	8
Mg_2 Si	$A^{II}B^{IV}$	8	1	0	8
Ga_2Te_3	$A^{III}B^{VI}$	24	3	0	8
SiC	$A^{IV}B^{VI}$	8	2	4	8

2) Dual-phase semiconductor comprise elements of IVA – VIIIA subgroup of the periodic system.

3) Most of semiconductor phases of IVA – VIIA elements obeys to the normal valence law

$$xA = y\,(8\text{-в}) \qquad (3.58)$$

where A and B are respectively the valence of elements A and B in the $A_x B_y$ compound.

A and B components included in the compound by ratio X:У. For example: InSв: $A_{In} = 3$; $B_{Sв} = 5$; 1 * 3 = 1 * (8-5)

4) The difference between the electronegativities of ΔX elements included in the dual semiconductor phase is usually not small.

ΔX characterizes the ability of atom in the crystal (molecule) to attract valence electrons.

The amount of ΔX is proportional to $\sqrt{\Delta}$: $\Delta X \sim \sqrt{\Delta}$, where

$$\Delta = E_{A\text{-}B} - (E_{A\text{-}A} + E_{B\text{-}B})/2 \qquad (3.59)$$

$E_{A\text{-}A}$, $E_{A\text{-}B}$, $E_{B\text{-}B}$ – binding energy between A-A, A-B, B-B atoms.

Physically, the magnitude of Δ is similar to the value of the interaction parameter Ω.

If the binding energy expressed in electron volts per atom, then

$$\Delta X = \frac{0{,}2}{\sqrt{\Delta}} \qquad (3.60)$$

Note that, in general case, with increasing ΔX increases proportion of ionic component of the bonding.

§ 8. Deviations from equilibrium state. The phase equilibrium diagrams role in selecting the conditions of crystallization and thermal treatment

Liquation. (Liquation- melting, smelting, in metallurgy – (segregation) – inhomogeneity of chemical composition of the alloys occurs at crystallization because the alloys unlike pure metals do not crystallize at the same temperature and in the temperature range). Discussed earlier phase transformations are in equilibrium at given temperature. That is, the rate of temperature change is so small that at any given temperature, time to make all atomic motion associated with the change in the chemical and phase composition, dictated by the particular phase equilibrium diagram.

However, these atomic movements carried out by diffusion takes time, the duration of which depends primarily on the nature of diffusing element, environment, temperature, size and perfection of the crystals, and other factors. In real conditions time required to reach equilibrium state may be different; by seconds or even fractions of second to many hundreds of hours. This explains the fact that in practice rarely observed equilibrium phase state. Moreover, such conditions are attained with difficulty, the same rule will be deviations in varying degrees from the equilibrium state.

The most common example of this deviation is the *liquation, which consists in the fact that chemical composition of the volume of crystal (ingot), solidified the beginning of crystallization is different* *from the volume composition, crystallized in the last turn.* To eliminate liquation using extended high-temperature heating (homogenizing annealing), but it is not always achieves equilibrium-alignment structure over the entire crystal (ingot). Apply special methods of crystallization to obtain crystals with uniform distribution of impurities.

Let us consider liquation phenomenon on the example of solid solutions formation. Liquation due to the fact that in any temperature of crystallization solid phase differs in composition from the liquid. The degree of this difference is characterized by the distribution ratio. Under equilibrium conditions $k_0 = C_S/C_L$.

In Fig. 3.16 shown liquation on the example of alloy with $k_0 < 1$. Consider continuous crystallization of alloy *r* with composition C_0 while cooling within temperature range of crystallization. In accordance with phase diagram at the starting temperature of crystallization it should appear crystal composition *a,* at temperature T_1 – crystals with composition *b,* at T_2 – with composition *c* and etc. Thus, with decreasing temperature layers are formed of solid phase enriched in impurity component *B*.

In conditions of equilibrium crystallization solids content corresponding to each value of temperature should be the same over the whole volume, and not only in layers, which crystallized at given temperature.

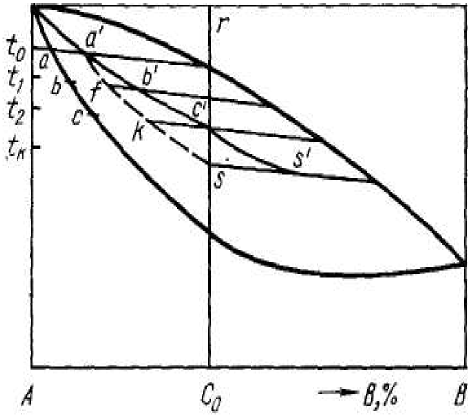

Figure 3.16. – Sceme of liquidation in alloys systems with unlimited solubility of the components.

To comply these conditions it is necessary:

a) in solid phase can travel diffusion alignment of composition layers of early and late crystallization;

б) to have time to go through diffusion alignment in the liquid phase. The last requirement is due to the fact that during the crystallization at $k_0 < 1$ layer of liquid melt, which adjacent to the crystal surface enriched by impurity, as it were "stripped" crystal into the melt, because $C_S < C_L$, while in real conditions or crystallization alloys with $k_0 < 1$ the effective distribution coefficient (k_{ef}) more than equilibrium distribution coefficient (k_0). In the real conditions diffusion alignment in the solid phase because of significant cooling rate never goes completely, and crystallization goes on the non-equilibrium solidus. If we accept that in liquid phase has time to go through the composition alignment, non-uniform composition of solid solution is characterized by average concentration, which lies to the right of the line of non-equilibrium solidus *a's'* – in our scheme on the dotted line of *a's*. Thus, when temperature T_1 solids content instead of *b'* is the average between *b'* and *a'*, and will correspond to the point *f*; at T_2 –respectively to *k* point, average between *b'* and *c'*, and etc. In conditions of non-equilibrium crystallization change not only the position of the solidus curve, but also the position of the liquidus curve.

Thus completion of crystallization will not occur when non-equilibrium solidus temperature T_2, and at temperature T_c, when the average composition of solid phase lying on *a's* line's, would be equal to C_0.

If you put on the diagram the actual end point of crystallization for alloys of different composition under specific cooling conditions, we obtain line, which is called non-equilibrium solidus for selected conditions (*a's* line in Fig. 3.16). Decreasing the temperature of crystallization ending by increasing the cooling rate leads to the fact that in the case of alloys which form continuous series of solid solutions, the crystallizing composition of the latter portions of melt is close to the composition of the second (low-melting) component *B*.

As result, the non-equilibrium crystallization of crystal chemical composition of the cross section is non-uniform. If crystallization occur with large supercooling, i.e. at temperatures much lower than the equilibrium temperature of the onset of crystallization, the solidification front is obtained is very uneven, crystals grow in the form of **dendritic** (tree-like formations). "Axes" of dendrites crystallizes first if they contain fewer impurities than the crystal region solidify last. This phenomenon is called the *intracrystalline* or *dendritic liquation.* Different chemical composition of the alloy causes different effects on chemical etching, which allows to good identify intracrystalline liquation using metallographic methods (Fig. 3.17).

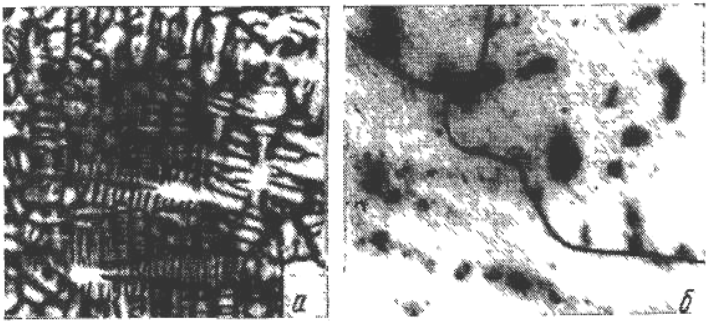

Figure 3.17. – Microstructure of the alloy with traces of dendritic crystallization before (*a*) and after (*б*) annealing.

Above it was assumed that the alignment of liquid phase composition in the crystallization process go to completion. However, in practice and it is not possible to observe because of the following reasons. Aligning the melt composition is carried out primarily by diffusion. The effectiveness degree of this process depends on the rate of diffusion of impurities in the melt, cooling rate, and the distribution coefficient. Furthermore diffusion for composition alignment can create convection currents in the melt by stirring. However, in this case the travel speed of melt layer directly adjacent to the surface of solid phase is very small, and only way to the composition alignment structure in this layer is diffusion.

As noted, among other factors on the effectiveness of melt composition equalization influences the cooling rate. With its increasing equalization process in liquid solution will be more suppressed. At very high speeds the cooling diffusion redistribution of different types atoms in the melt is not possible. Under these conditions, the crystallizing composition of solid solution will be equal to the composition in liquid phase. This process is called ***diffusionless*** crystallization. Obtaining alloys by such method have practical interest.

Deviations from equilibrium state, even more sharply than in systems with unlimited solubility, achieved in conditions of accelerated cooling systems with eutectic and peritectic transformations.

Thus, in systems with eutectic alloys, single phase in equilibrium crystallization conditions may be two-phase in non-equilibrium crystallization conditions. The consequences of such non-equilibrium crystallization under favorable conditions, can be shot long leveling (homogenizing) annealing (Fig. 3.17 *б*).

Metastable phases. EPD with metastable phases.

Another important example of deviation from equilibrium is formation of *metastable phases* in the phase transitions process. So called non-equilibrium phase, which are in some cases:

а) transitional stage between initial and equilibrium phase,

in others -

б) phase stable at certain pressure, temperature and concentrations ratios.

On the phase equilibrium diagram of **metastable equilibrium depicted by dashed lines.**

Metastable phases formed by crystallization of elementary substances and binary alloys with considerable supercooling of the melt (solution), temperature and concentration range in which the phases are metastable, has different length. Isobaric-isothermal potential of the metastable phase is less than in original, but greater than in the equilibrium phase, so the transformation of the metastable phase to equilibrium requires certain activation energy, absence of which the metastable phase can exist indefinitely.

Formation of metastable phases – phenomenon often observed and widely used and transformations in the solid state. This includes, above all, the formation of supersaturated solid solutions, if their decay is carried out at low temperatures, when the diffusion and thus the formation of the equilibrium phases difficult.

There is every reason to believe that observed in heavily doped semiconductors concentration mismatch of electrically active impurity and its overall (chemical) concentration *(polytropic impurities)* is in many cases the result of the initial stages of solid solution decomposition, in which the impurities are formed with the participation of metastable phases.

Metastable phases are also formed in sharp cooling of solid solutions that have at equilibrium cooling experience eutectoid transformation. An illustration of this is the martensitic transformation during quenching of steel (austenite). Many of metastable states cause the alloys useful and sometimes unique properties. The aim of material science – establishment of the nature of these non-equilibrium states and development of the fundamental mode, which allows to obtain metastable state. The starting point for solving these problems is the knowledge of phase equilibria diagrams.

For description of metastable phases using special equilibrium phase diagram of metastable phases – the so-called metastable diagrams. *Region of the metastable and metastable chemical compounds on these diagrams shown by dashed line.* The question about application of the phase rule to metastable diagrams is debatable. In Fig. 3.17 (2) shown the equilibrium phase diagram of Co-C and Ni-C systems and metastable diagrams of these systems.

The value of metastability is determined by the difference between the energies of metastable phase and mixture of stable phases. At very high cooling rates (10^2 – 10^{10}) K/s of supercooled melts (solutions) below certain temperature can be obtained solid metastable phase not only in crystalline but also in amorphous state (when phase has short-range order, and has not got long-range order in the arrangement of atoms). Alloys in amorphous state can be obtained not only during the crystallization from the liquid phase, but also during the deposition from the gaseous phase. For obtaining amorphous phases with covalent type of bonding requires lower cooling rate compared with the metallic bonding type of phases.

Knowing the phase equilibrium diagram is also necessary in the case of choosing liquid phase composition and temperature conditions of crystallization. This is particularly important in the preparation of crystal compounds. Let's consider on the example of producing single crystals by pulling them from the liquid phase by Czochralski method.

Crystallization occurs at the seed-crystal, which in contact with the surface of molten liquid, supercooled to ΔT below the liquidus temperature. This supercooling is maintained throughout the crystallization process. As crystallization of solid phase new layers on seed crystal pulled from the liquid phase. The composition of crystallizing solid phase is determined by the phase equilibrium diagram, if in the process of drawing support conditions close to equilibrium (crystallization rate is small, wide spread diffusion processes in the solid and liquid phase, i.e. $\Delta T \to 0$).

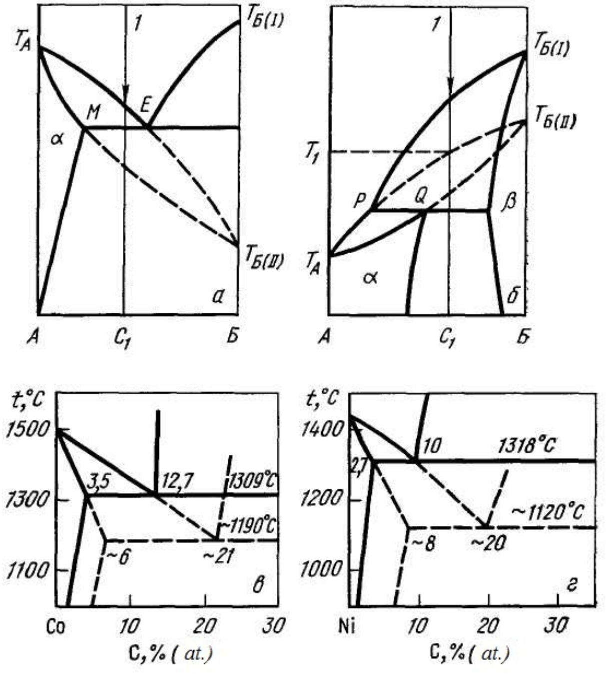

Figure 3.17 (2). – Metastable diagrams (solid lines – stable, dashed lines – metastable equilibrium):

а – possible metastable equilibrium in the diagram of eutectic type;

б – possible metastable equilibrium in the diagram of peritectic type;

в – metastable diagram of the Co-C system;

г –metastable diagram of the Ni-C system.

Congruently melting compounds, e.g. GaTe and Ga_2Te_3 (see. Fig. 3.13 *a*) can be obtained from the liquid phase of the same composition as compound. They can be prepared by crystallization from the melt and slightly different composition: for example, compound GaTe – from melt composition X_1 crystallization at temperature in the range of between 1100 and 1019 K. However, it should be noted that if compound has certain homogeneity, then pulled crystal will not have stoichiometric composition, and will be solid solution with limit concentration based on the compound, the equilibrium temperature for crystallization.

Incongruent melting compound can not be obtained from the liquid phase of the same composition. Thus, in Fig. 3.13 shown that from the liquid phase corresponding in composition to $GaTe_3$ at supercooling below the liquidus line will crystallize Ga_2Te_3, solid phase composition, but not $GaTe_3$. During the crystallization from the liquid phase allocated congruently melting compound $GaTe_3$, liquid phase composition should lie in the range of concentrations from X_2 to X_3, and crystallization should be carried out at temperature between T_3 (~760 *K*) and T_4 (709 *K*). Consideration of the above crystallization incongruent melting compound called as ***crystallization from solution***.

In contrast from this crystallization from the liquid phase corresponding to the composition of crystallizing solid phase, called the ***crystallization from the melt.*** In general, the concept of "melt" and "liquid solution" require clarification. Under ***melt*** should be understood liquid phase having composition on the main (primary) component (components) corresponding to the composition of elementary substance or compound within the accuracy of their determination, and contents of background impurities and dopants, which does not exceed (1 – 2)% (atom). Under ***liquid solution*** to be understood liquid phase, the composition of the main components of which does not coincide with the composition of solid phase, as well as liquid phase, the contents of background impurities and dopants which exceed (1 – 2)% (at.).

§ 9. P – T and P – T – X diagrams of phase equilibrium

The use of high and ultra-high pressure (several tens of GPa) in number of cases leads to change in the type of phase diagram, dramatic shift of the phase transformation temperature, appearance of new phases that are not in the system at atmospheric pressure. Importance of studying the phase equilibrium diagram, constructed in the $P - T - X$ coordinates (where P –external pressure) connected with this.

Thus the basic regularity is difficult that pressure increasing impede to the conversion, connected with increase of the specific volume, and expands on the composition and temperature of the existence region of phases with high density.

Due to the increased role in semiconductor electronics of various kinds of semiconductor compounds and solid solutions based on them, containing volatile components have interest to study the phase diagram, constructed in the $p - T - X$ coordinates, where p – vapor pressure of volatile component or pressure of its dissociation.

In systems which components have low dissociation pressure, and in which the maximum melting temperature of mixture below the lowest boiling temperature of component, the role of gaseous phase can be neglected. Phase diagrams for these systems is typically built to temperatures below the boiling temperature.

In Fig. 3.18 is given example of phase diagrams with eutectic at temperatures below the boiling point of pure components.

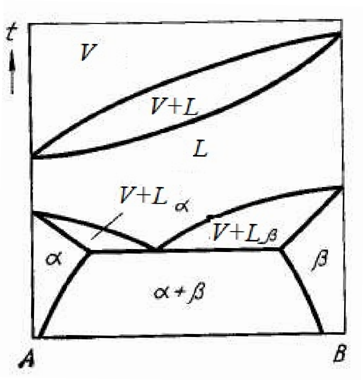

Figure 3.18. – Phase diagram of system with eutectic gap of solubility and low pressure of components dissociation

If the dissociation pressure of any component is large, the composition of gaseous phase must be considered at temperatures both above and below the liquidus temperature substantially throughout the range of temperatures, which investigated the phase equilibria in the studied system.

Thus, one should distinguish phase diagrams for systems with low pressure dissociation in which P – external pressure affecting, in particular, on the phase transformation in the solid state, and for systems with large dissociation pressure, in which p – vapor pressure of volatile component or dissociation pressure; we denote it by p_{dis}. The main feature of these phase diagrams is the appearance of geometric elements that describe the composition of gaseous phase.

Phase diagrams constructed in the P – T coordinates.

Diagrams of single component system presented in the *P–T* coordinates are diagrams projection constructed in the G–T–P coordinates (where *G* –isobaric-isothermal potential) on the plane *P–T* (Fig. 3.19). *G–T–P* diagrams demonstrate the equality of chemical potentials of the component (or adequate to it in single-component system – isobaric-isothermal equality potential phase) under phase equilibrium.

P–T diagrams are phase diagrams of one-component systems, in which the phase transformation caused only by changes in temperature and pressure.

P-T diagrams of substances which do not undergo polymorphous transformation in the solid state, shown schematically in Fig. 3.19, *б*, *в*. The phase regions corresponding to solid, liquid and vapor state, separated by monovariant two-phase equilibria lines: *OA* –curve of sublimation; *AC* –melting curve; *AB* –curve of evaporation (boiling), along with ongoing equality:

$G_S = G_L$ or $G_L = G_V$

or

$\mu_S = \mu_V$, $\mu_S = \mu_L$ or $\mu_L = \mu_V$.

Point *A* is non-variant and corresponds to the three-phase equilibrium.

Task. Determine the number of freedom degrees at point *A,* Fig.3.19.

The diagrams in Fig. 3.19, *б*, *в*, different slope of the melting curve *AC.* The slope of each of the two curves is determined by the sign of the derivative dT_m/dP, which in turn is determined by the sign change in the specific volume of the phase transition type.

Increasing the pressure increases temperature of phase transformation, if it is accompanied by increasing in the specific volume and decreases this temperature, if during the phase transformation process specific volume decreases.

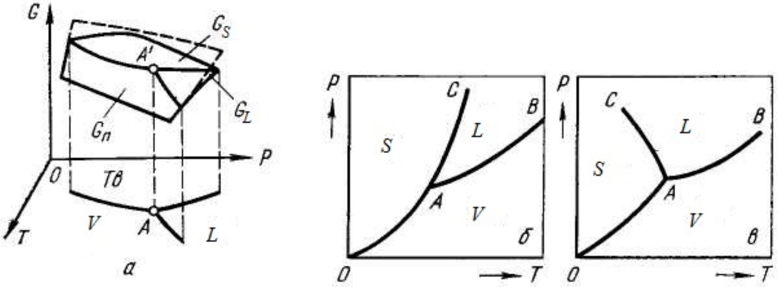

Figure 3.19 – Phase diagram of one-component system:

a – diagram built in *G–T–P* coordinates; said surface isobaric-isothermal potential *G* of the individual phases of the two lines of intersection of these surfaces meet monovariant, and the point of intersection of three surfaces – non-variant phase equilibrium; *б*, *в* – diagram constructed in *P–T* coordinates, while the melting of solid phase is accompanied by increasing (*б*) and decreasing (*в*) of specific volume

Thus, at $dV/dT > 0$ and $dT/dP > 0$ phase transformation line tilted to the right, and at $dV/dT < 0$ and $dT/dP < 0$ – to the left.

Evaporation and sublimation are always accompanied by increase in the specific volume, so the curves *OA* and *AB* are always inclined to the right.

The sign change of specific volume and, hence, the density in the melting is ambiguous. If melting of metals ΔV is always positive (Fig. 3.19, *б*), then in the case of melting semiconductors sign of change ΔV depends on whether the transition is accompanied by liquid state change in the nature of chemical bondings or not.

Upon melting of semiconductors, the following two cases of transition from solid to liquid are possible:

1) semiconductor → semiconductor

2) semiconductor → metal.

In the first case, typical of such substances as sulfur, selenium, tellurium, compounds of Bi_2Te_3, Cu_2S, some compounds of $A^{II}B^{VI}$ type (e.g. CdTe), $\Delta V > 0$, at the second characteristically for germanium and silicon, as well as for number of compounds of $A^{III}B^{V}$ type, on the contrary, $\Delta V < 0$ (Fig. 3.20).

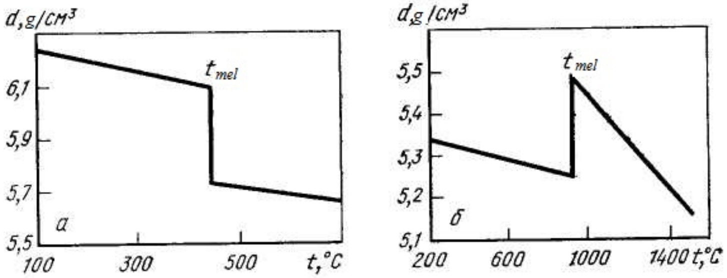

Figure 3.20. – Change the density in the melting of semiconductor materials:
а –tellurium (at melting stored covalent p^2–bondings)
б – germanium (in the melting destroyed covalent sp^3–hybrid bondings).

The decrease in the specific volume in the melting of semiconductors due to the fact that the characteristic of covalent bondings non-compact packing of atoms in diamond or sphalerite-type lattice replaced by more compact package with large coordination number, characteristic for metallic materials.

Thus, high pressure increases the melting point of metals and increase it at some semiconductors.

P – T diagrams of substances tested in the solid state polymorphic transformations.

In Fig. 3.21, *а* shown *P–T* diagram for SiO_2, having in solid state large number of polymorphic modifications (including α-quartz, β-quartz, tridemit, cristobalite).

In Fig. 3.21, *б*, *в*, *г* shown *P–T*- diagrams of germanium, silicon, carbon. Using pressures above 10^{10} Pa shown that under such pressures diamond-type lattice with the coordination number *K = 4* goes into the lattice of the higher coordination number *K = 6,* but instead of covalent chemical bonding becomes metallic.

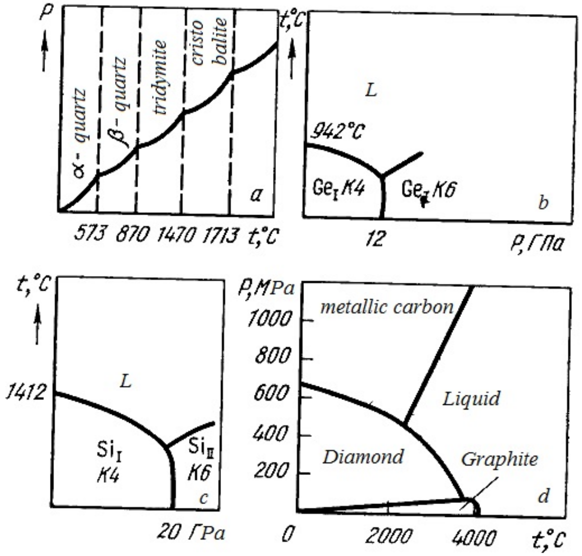

Figure – 3.21. *P – T –* diagrams of one-component systems undergoing polymorphic transformations: *a* – SiO_2; b – Ge; *c* – Si; *d* – C

In some cases polymorphic transformation caused by high pressure may be practically irreversible. Then it is possible, once subjected to high pressure agent, get it under normal conditions in metastable state with unusual properties for these conditions.

Phase diagrams constructed in the P – T – X coordinates

In Fig. 3.22 *a*, shown hypothetical *P–T–X*- diagram of the binary system. The change in pressure can lead to change, not only the temperature of phase transformation, but also change type of phase diagram. Thus, the diagram of unlimited solubility in the solid state at high temperatures, and separation of the solid solution α to two solution at low temperatures with increasing pressure gradually changes to the diagram with eutectic. This transition appears, it must correspond to the case when the initial volume of solid solution α is greater than the total volume of phases $\alpha_1 + \alpha_2$, formed from the same amount of starting substance[4].

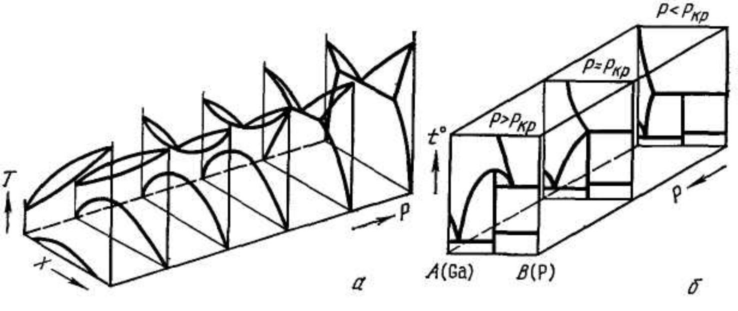

Figure 3.22. *P–T–X* –diagrams of systems without the formation (*a*), and formation of GaP chemical compound (*б*) (compound of $A^{III}B^{V}$ type) include easily volatile component (phosphorus)

In Fig. 3.22, *б* shown phase diagram of Ga-P, which produces GaP semiconductor compound. Depending on the pressure, this compound can be melted congruent or incongruent. Accordingly, to changes and view of dual *T-X* on various isobaric sections of the triple *P-T-X* – diagram.

These examples show that between the different types of diagrams have sharp boundaries and that system diagram of these components depending on the external conditions can change from one type to another.

Volume *P-T-X* – diagrams similar to those shown in Fig. 3.22 build very rarely. Typically, phase transformations in three-dimensional *P-T-X* – diagrams are analyzed by their projections on the plane *P–T*, *T–X* and *P–X*, as well as use different sections at constant temperature and pressure (*P–X* – and *T–X* – section).

These projections build in accordance with the laws of descriptive geometry (Fig. 3.23 and 3.24). In their analysis must take into consideration that for the system in Fig. 3.23 dissociation pressure is small and *P* –the external pressure, and in the In-As system in Fig. 3.24

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[4] Example is solid solution of carbon in iron with tetragonal distorted lattice – the so-called martensite. The collapse of martensite into two phases – less concentrated solid solution of carbon in iron with BCC lattice and iron carbide Fe_3C (cementite) – accompanied by decrease in volume.

pressure dissociation of arsenic is high and in this case $P = p_{\text{disAs}}$ where p_{disAs} – equilibrium conditions for these pressure dissociation of arsenic (in the general case should be considered p_{disAs} of all phases in equilibrium).

General regularities of the influence of pressure on the phase states as follows:

At high pressures of dissociation gaseous phase is stable, the condensed phase does not exist. Therefore, under these pressures is the boundary that separates the regions of existence of gaseous and condensed phases.

To two-phase equilibrium corresponding surfaces, limiting the adjacent single-phase region.

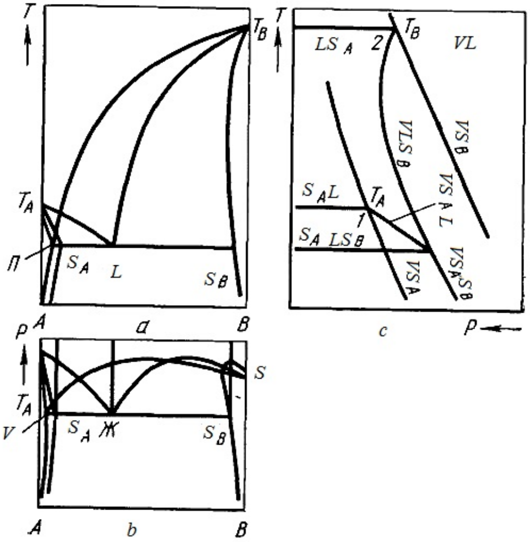

Figure 3.23. – Projections P_{dis}–T–X – diagrams of two-component systems with eutectic break solubility:

a – to the plane *T-X;*

б – to the plane *P-X;*

e – to the plane *P-T.* Symbols on the lines denote the phase equilibrium under these conditions. Points 1 and 2 correspond to the three-phase equilibrium of pure *A* and *B* components

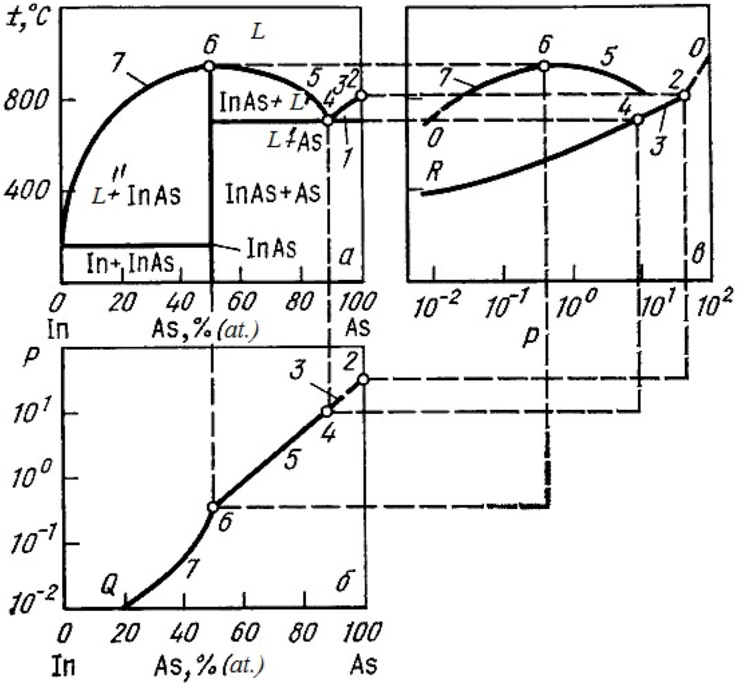

Figure 3.24. – Projections of $P_{дис}$–*T*–*X*-diagram of In–As system: *а* –to the plane *T-X; б* – to the plane *P-X; в* – to the plane *P–T*.

The points on the projections correspond to the equilibrium between the phases:

2 – As_S+As_L+As_V; *4* – InAs + As eutectic; *6* – InAs+*L*+*V*; *7* – InAs+*L*"+*V*; *L*' и *L*" –composition of the liquid solution with excess (compared to stoichiometric) of arsenic and indium, respectively.

Equilibrium of three phases in P–T – projection correspond to the line, four-phase equilibria are projected on P–T – projection as points at which intersect lines of three-phase equilibrium.

On *P–T* –projections often applied also two-phase line and triple point of pure components (see. Fig. 3.23). As noted above, p_{dis}–*T*–*X* – diagrams extremely important for systems containing semiconductor compound composed of volatile components, such as phosphorus and arsenic in $A^{III}B^{V}$ compounds. Among the components, which incoming in $A^{II}B^{VI}$ (CdS, HgTe) compound type, high pressure dissociation possess not only the anions of sulfur, selenium and tellurium, and some cations, for example cations of mercury and cadmium.

As noted above, all semiconductor compounds have more or less extended homogeneity range, i.e. capable dissolve any type of component over stoichiometric composition or "third" component - vacancy.

Any deviation from the stoichiometric composition greatly affect to the electro-physical properties. Therefore, for obtaining stable crystals with desired properties must be stable obtaining crystals of the compound in given composition. The last task is impossible, if p_{dis}–T–X – diagram of appropriate system is unknown. This is due to the fact that the volatility of one component results in the formation of vacancies – anionic and cationic (depending on the dissociation pressure of the component will be larger), and accordingly to excess of another component. In number of compounds vacancy created acceptor or donor levels, affecting to the electro-physical properties. Number and position of the levels depend on the chemical nature of the element replaced by vacancies, composition of compounds, and others.

The energy of vacancies formation in the A and B positions are never the same, so the concentration of anionic and cationic vacancies is also different, and the homogeneity region of the compound is asymmetric with respect to the stoichiometric composition. Consequently, for such compounds maximum of melting temperature does not correspond to the stoichiometric composition of the alloy, i.e. compounds formation with shifting stoichiometry.

To prevent changes in the composition of compound due to volatility of components is possible, if it is grown from the melt or solution under external pressure of the volatile component, which is equal to the dissociation pressure at growing temperature. These conditions are selected by p_{dis}–T–X diagram.

CHECKLIST AND TASKS

1. What are the characteristics of metals and semiconductors determine the temperature dependence of conductivity?

2. What caused the nonlinearity of certain optical and acoustic properties (absorption, scattering, diffraction, etc.) from the intensity of irradiation exposure?

3. How does the type of chemical bondings in solids influence on their properties (mechanical, electrical, acoustic, and others.)?

4. Why is tungsten not ferromagnetic?

5. Why is silicon not used as structural material?

6. Silicon and germanium form continuous series of solid solutions. Determine the compactness coefficient of crystal lattice of the $Ge_{0,5}Si_{0,5}$ solid solution composition and bandgap of the solid solution.

7. Determine the concentration of valence electrons and conduction electrons in monocrystal of n-type silicon at 300K, if it is known that the electrical resistivity is 10^5 ohm*cm, and the electron mobility is 1400 cm^2 / (V*s).

8. Determine binding energy of the silicon crystal in kilojoules per atom.

9. Why for growing monocrystals of silicon, as well as other diamond-like phases, mainly used containerless crystallization methods, such as Czochralski method?

10. Determine ΔS_m melting entropy of iron, tungsten, silicon, germanium and tellurium and compare the values obtained with the nature of changes of the chemical bondings of these substances during melting.

11. Draw unit cell of solid solution containing 50% (at.) Ge and 50% (at.) Si. In two cases: in the presence of ($\eta = 1$) or in the absence of ($\eta = 0$) short-range order.

12. Build P–T – projection of two-component phase diagram of A–B system, in which produces one congruently melting compound AB twoside region of homogeneity. Compound AB and component B have high pressure of saturated vapor. At the P–T –projection apply the line of three-phase equilibria.

13. Name the compounds with shifted stoichiometry among the compounds $A^{IV}B^{VI}$.

14. Why can not get SnTe compound of n-type conductivity without doping by third component?

15. Can we get monocrystals of PbS and SiC compounds from melts corresponding to the stoichiometric composition?

16. Why does bandgap of GaAs compound smaller than in AlSb compound?

17. Which will of this two compounds GaAs and Ga_2Te_3 more radiation-resistant?

18. In the range of what atomic masses $A^{III}B^{V}$ and $A^{II}B^{VI}$ compounds will have bandgap greater than 2 eV.

19. Why does as thermoelectric material is advisable to use not impure compound, but solid solution based on it?

20. What is the difference in behavior during heating of amorphous and glassy materials?

21. What is the difference of the structural characteristics of amorphous materials with metallic and covalent bondings?

22. Do $CuInSi_2As_4$ and $CuGaGe_2As_4$ compounds obey to rule of Mooseri-Pearson, which crystallize in the structure of sphalerite?

23. What are the similarities and what differences of crystallization, backboiling and recrystallization processes?

24. How and why different work homogeneous nucleation of new phase in the case of conversion to the solid state and in the case of crystallization from the liquid phase?

25. Does the saturated vapor pressure in the space above the particle (droplet) of the substance dependent only to the size (volume) or to its forms?

26. What does explain that the microstructure of polycrystalline ingot of silicon, germanium, copper characterized by large number of twins, and in the microstructure of aluminum there is practically absent?

27. What are the main types of phases can exist in solid?

28. The equilibrium state of system. Hetero – and homogeneous systems.

29. Phase. Allotropy (polymorphism).

30. Types of solid solutions. Components of the system (number of components)

31. Thermodynamic potentials. Opportunities of phase equilibria diagrams.

32. Phase transitions of the I-st and II-nd kind.

33. Conditions of heterogeneous equilibrium phases.

34. Gibbs phase rule.

35. The main presentations in the construction of phase diagrams of binary systems.

36. Thermodynamic functions describing the solution.

37. Isobaric-isothermal potential of shifting in the case two ideal solutions (liquid and solid) equilibrium.

38. T – X diagrams of phase equilibria of binary systems with unlimited solubility.

39. Application of solid solutions with unlimited solubility.

40. Construction of phase diagrams with unlimited solubility according to the data measurement of thermodynamic potential.

41. Transition from unlimited to limited solubility.

42. T – X diagrams of phase equilibria of binary systems with limited solubility.

43. Diagrams of phase equilibria with eutectic transformation.

44. Diagrams of phase equilibria with eutectoid transformation.

45. Diagrams of phase equilibria with peritectic transformation.

46. Diagrams of phase equilibria with peritectoid transformation.

47. Diagrams of phase equilibria with chemical compounds.

48. Diagrams of phase equilibria with eutectic with different chemical bondings of the components.

49. Liquation.

50. Dendrites.

51. Berthollides.

52. Daltonides.

53. General regularities of the influence of pressure on the phase states.

54. P – T diagrams of substances experiencing polymorphic transformations in solid state.

55. Growing methods of monocrystals.

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ATTACHMENT.
PHASE DIAGRAMS OF SOME SEMICONDUCTOR SYSTEMS

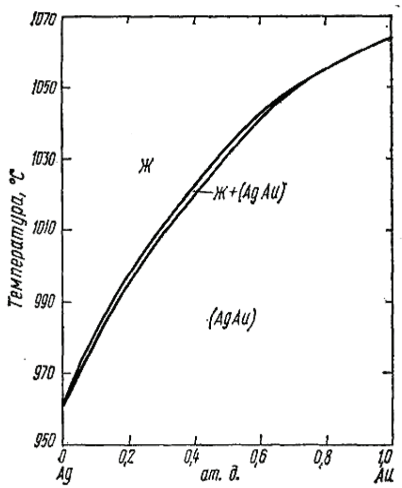

Fig. 1.
Phase diagram of the system
Ag – Fu

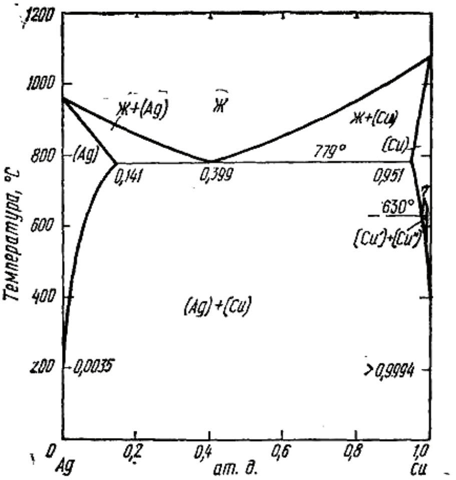

Fig. 2.
Phase diagram of the system
Ag –Cu

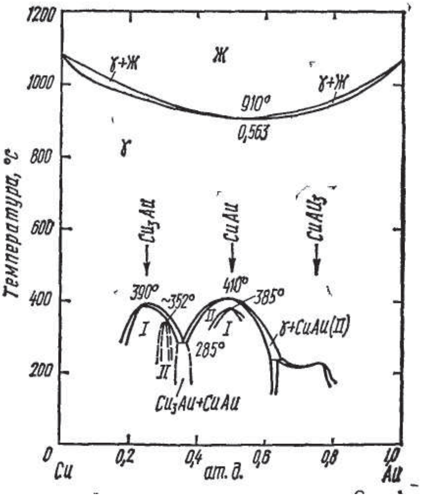

Fig. 3.
Phase diagram of the system
Cu – Au

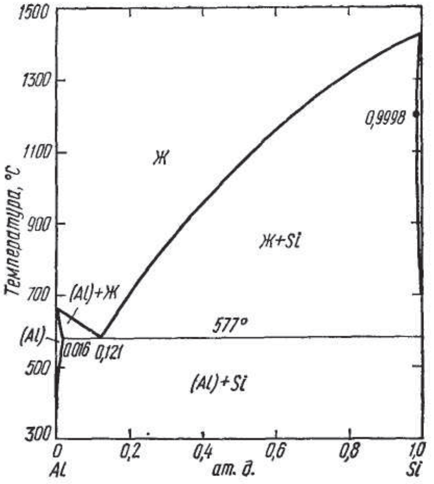

Fig. 4.
Phase diagram of the system
Cu – Fu

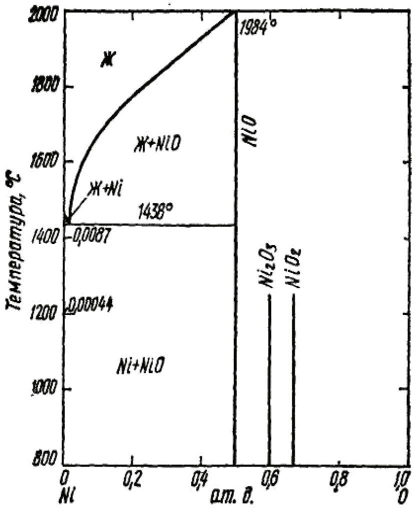

Fig. 5.
Phase diagram of the system
Nl – O

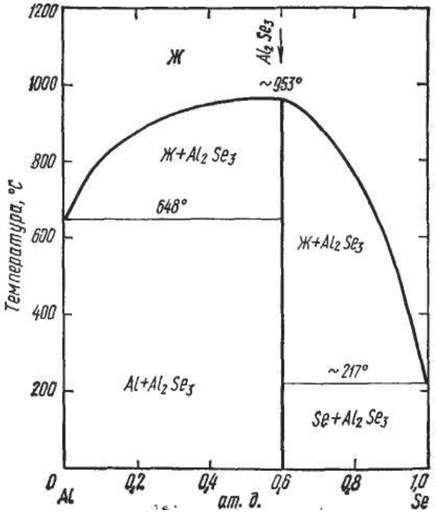

Fig. 6.
Phase diagram of the system
Al – Se

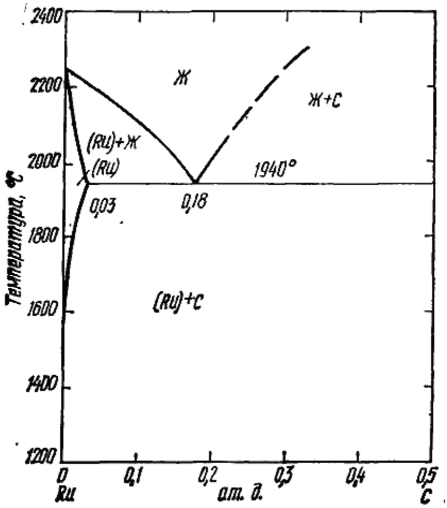

Fig. 7.
Phase diagram of the system
Ru – C

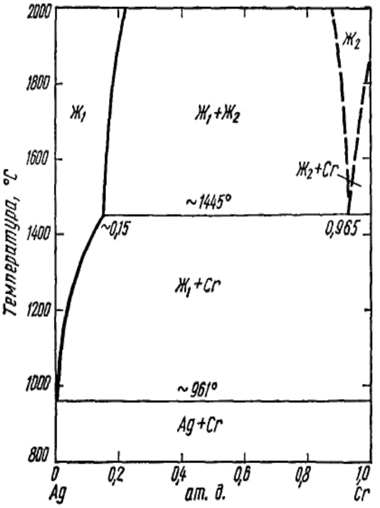

Fig. 8.
Phase diagram of the system
Ag – Cr

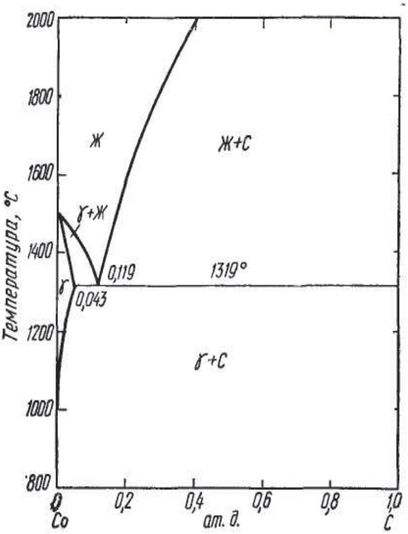

Fig. 9.
Phase diagram of the system
Co – C

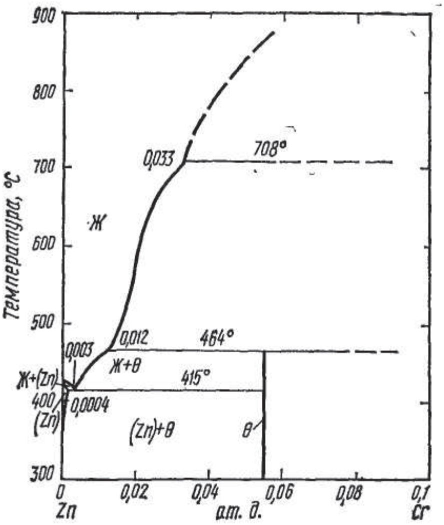

Fig. 10.
Phase diagram of the system
Zn – Cr

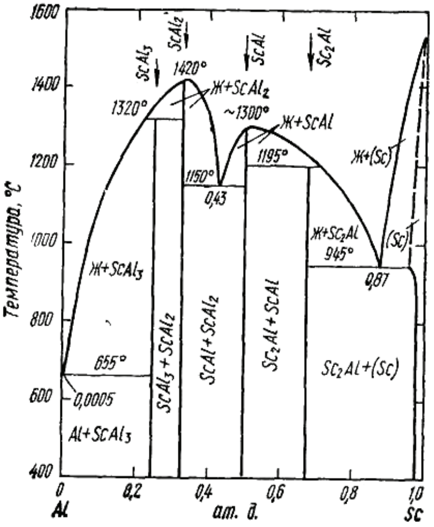

Fig. 11.
Phase diagram of the system
Al – S

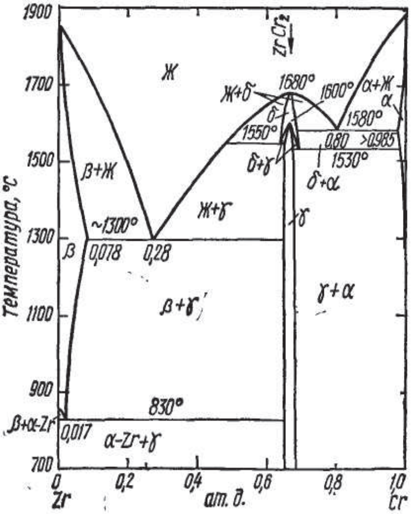

Fig. 12.
Phase diagram of the system
Zn– Cr

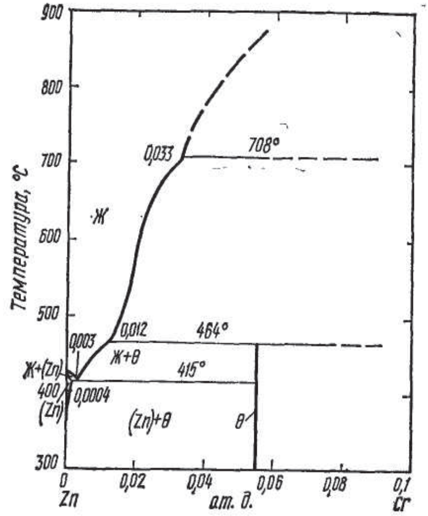

Fig. 13.
Phase diagram of the system
Zn– Cr

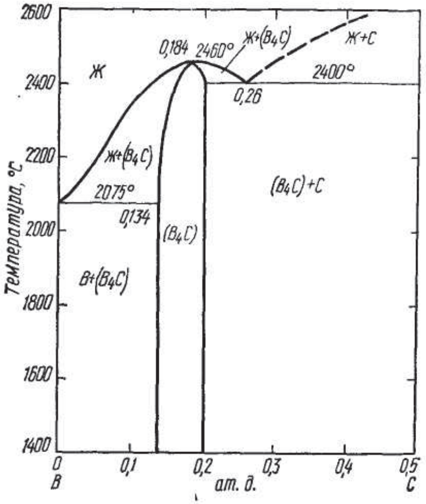

Fig. 14.
Phase diagram of the system
B – C

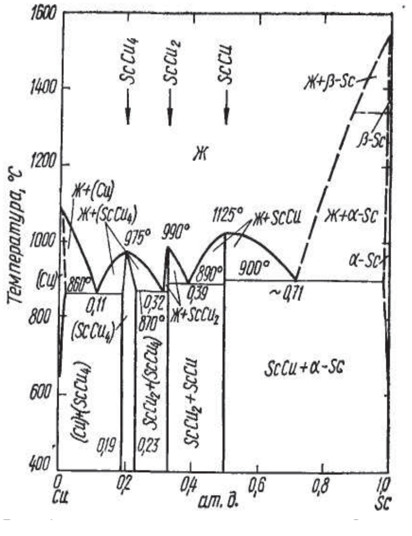

Fig. 15.
Phase diagram of the system
Cu– Sc

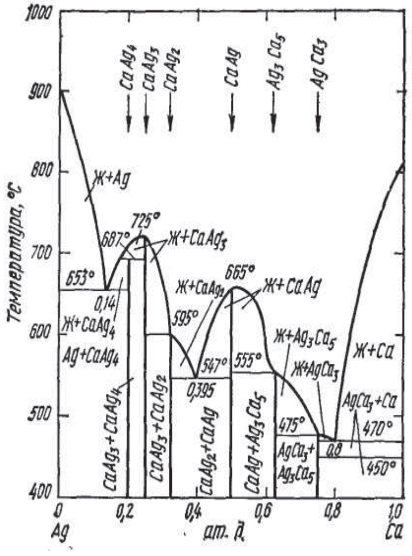

Fig. 16.
Phase diagram of the system
Ag – Ca

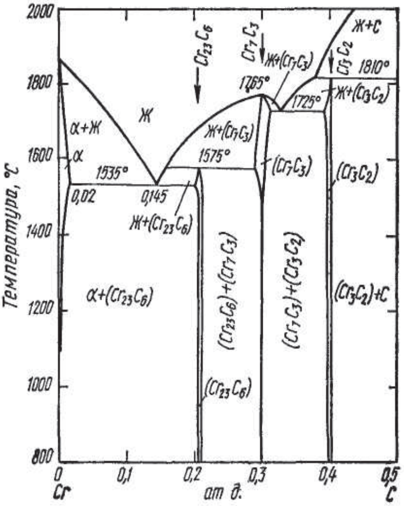

Fig. 17.
Phase diagram of the system
Cr– C

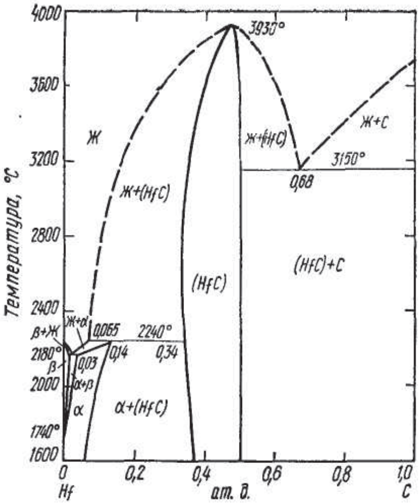

Fig. 18.
Phase diagram of the system
Hf – C

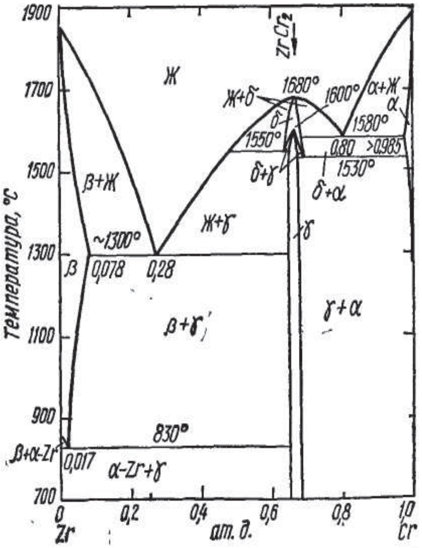

Fig. 19.
Phase diagram of the system
Zr– Cr

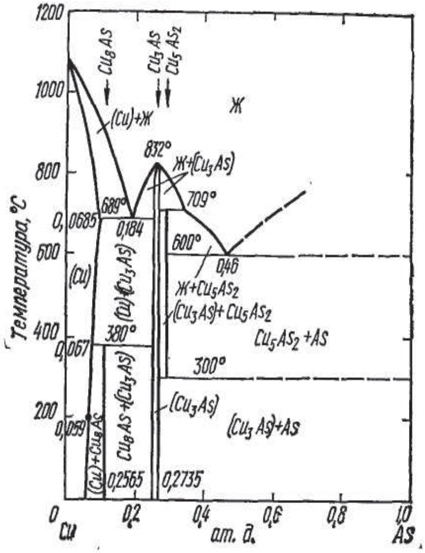

Fig. 20.
Phase diagram of the system
Cu – As

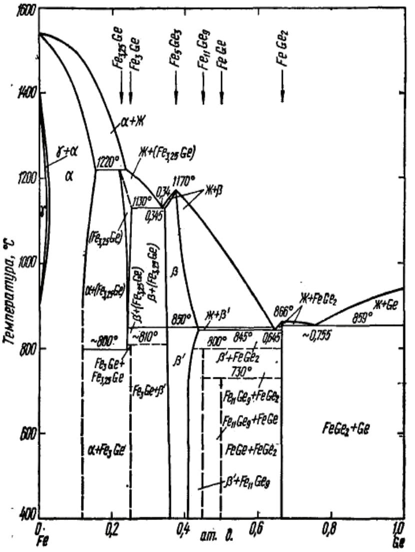

Fig. 21.
Phase diagram of the system
Fe– Ge

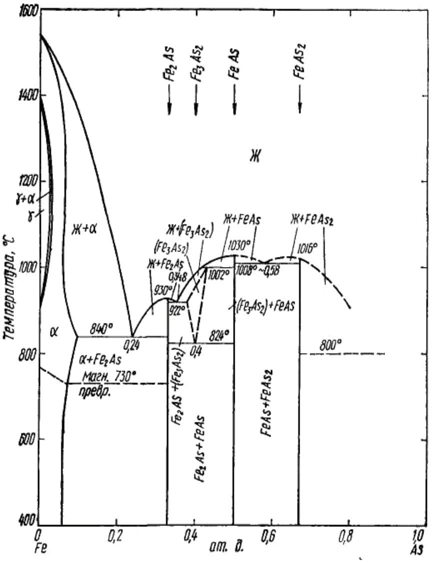

Fig. 22.
Phase diagram of the system
Fe – As

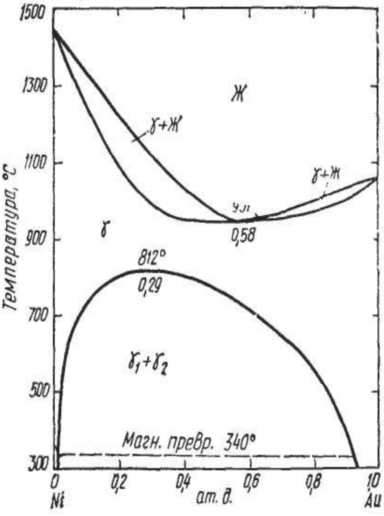

Fig. 23.
Phase diagram of the system
Ni– Au

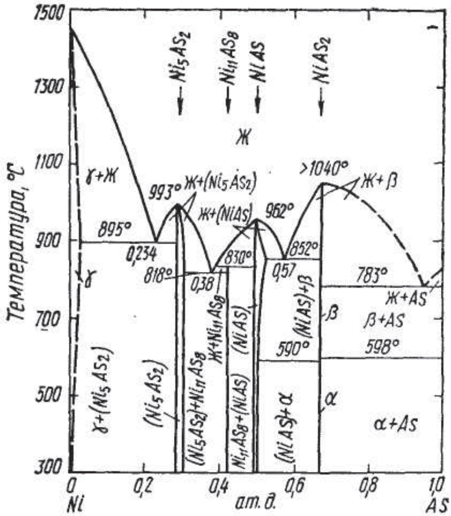

Fig. 24.
Phase diagram of the system
Ni – As

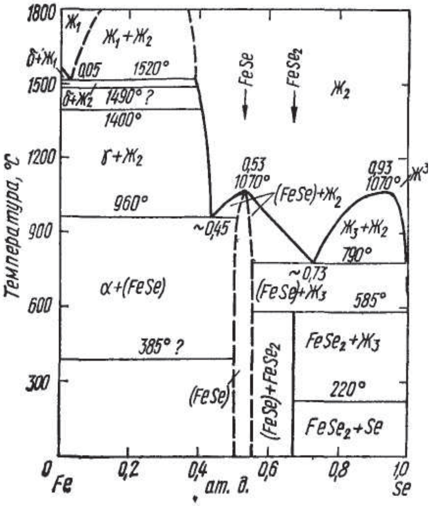

Fig. 25.
Phase diagram of the system
Fe– Se

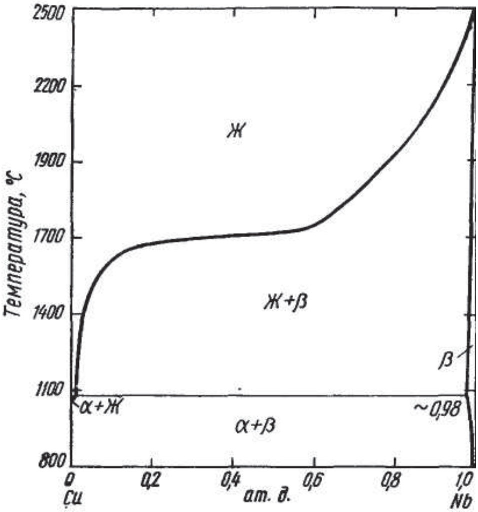

Fig. 26.
Phase diagram of the system
Cu – Nb

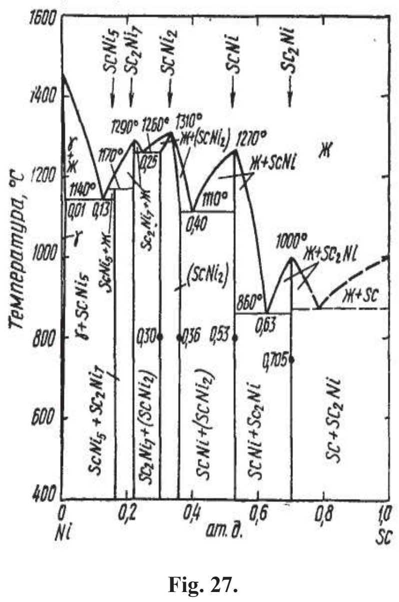

Fig. 27.
Phase diagram of the system
Cu – Se

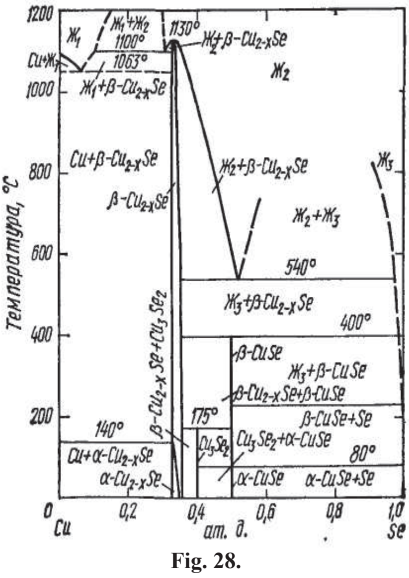

Fig. 28.
Phase diagram of the system
Ni– Sc

Учебное издание

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INTRODUCTION TO THE PHYSICAL MATERIAL SCIENCE

Education manual

Выпускающий редактор *Г.С. Бекбердиева*
Компьютерная верстка *Г.К. Шаккозовой*
Дизайн обложки: *А.Калиева*

ИБ №9991
Подписано в печать 22.12.2015. Формат 60х84/16.
Бумага офсетная. Печать цифровая. Объем 11,7 п.л.
Тираж 50 экз. Заказ № 3985. Цена договорная.
Издательский дом «Қазақ университеті»
Казахского национального университета имени аль-Фараби.
050040, г. Алматы, пр. аль-Фараби, 71, КазНУ.
Отпечатано в типографии издательского дома «Қазақ университеті».

«ҚАЗАҚ УНИВЕРСИТЕТІ» БАСПА ҮЙІНІҢ ЖАҢА КІТАПТАРЫ

Исатаев С.И. және т. б. Физикалық гидро- және аэродинамика: арнайы физикалық практикум. – 2015. – 192 б.
ISBN 978-601-04-1576-8

Физикалық гидро- және аэродинамика физика және техника мамандықтарының студенттеріне арналған арнайы физика курсы бойынша қолданыстағы университет бағдарламаларына сәйкес жасалған және 20 зертханалық жұмыстың сипаттамасынан тұрады. Әрбір зертханалық жұмыста қысқаша теориялық кіріспе, эксперименттік қондырғының сипаттамасы, жұмыс тапсырмасы, сондай-ақ эксперименттерді жүргізу әдістемесі мен олардың нәтижелерін өңдеу қамтылған.

Бұл арнайы физикалық практикумды жоғары оқу орындарында физика және физика-техника мамандықтары үшін пайдалануға болады.

Самбетбаева А.Қ. Ақпараттық жүйелерді талдау және логикалық жобалау: оқу құралы. – 2015. – 79 б.
ISBN 978-601-04-15-68-3

«Ақпараттық жүйелерді талдау және логикалық жобалау» оқу құралы «Ақпараттық жүйелер» мамандығы бойынша білім алушы студенттерге арналған.

Оқу құралында теориялық материалдар, жаттығулар келтірілген. Оқу құралында CASE-технологияларды жүйелік талдау мен қолдану қағидасына негізделген ақпараттық жүйелерді жобалаудың әдістемелік негіздері қарастырылған. Оқу құралының мазмұны ақпараттық жүйе- лерді жобалаудың мақсатынан, есептерінен, функцияларынан, құрылымынан, жобалау тәсілдері мен технологияларынан, жобалау сапасын бағалау мен басқарудан тұрады. Оқу құралындағы тест сұрақтары студенттердің алған білімін тексеруге мүмкіндік береді.

Сәрсекеева А.С. Математикалық физиканың теңдеулері: оқу құралы. – 2015. – 120 б.
ISBN 978-601-04-1561-4

Оқу құралында математикалық физиканың теңдеулері курсының негізгі тараулары бойынша теориялық материалдар қысқаша баяндалған және есептердің шығарылуы толығымен көрсетілген. Оқу құралында ішек тербелісі және жылуөткізгіштік теңдеудің шығарылуы, теңдеулердің классификациясы, оларды канондық түрге келтіру, теңдеулердің шешімін құрғандағы ең жиі қолданылатын әдістер – Даламбердің сипаттауыштар әдісі, Фурье әдісі, интегралдық түрлендірулер әдісі, Грин функциясының әдісі берілген. Әрбір тараудың соңында сұрақтар, жауабымен жаттығулар және өз-өзін тексеруге арналған нұсқаулар қамтылған.

Оқу құралы «Математика» мамандығының студенттеріне арналған.

Комаров Ф.Ф., Тоғамбаева А.К., Ақылбеков Ә.Т., Тоғанбаева Л.К. Материалдарды ионды және фотонды өңдеудің физикалық негіздері: оқу құралы. – 2015. – 272 бет.
ISBN 978-601-04-1596-6

Оқу құралында қатты денелер мен ионды шоқтардың өзара әсері физикасының заманауи түсініктері қарастырылған. Кристалдық тор дефектерінің пайда болуы және оларды босаңдату, байыту атомдарының берілген түрде үлестірілу профилдерінің қалыптасу процестері айқындалған. Материалды ионды және фотонды өңдеуге және ионды имплантанттালған қабаттардың қасиеттерін өзгертуге арналған заманауи техникалық құралжабдықтар жөнінде мәліметтер келтірілген. Заманауи микроэлектроника және қатты денелі электроника технологияларында ионды және фотонды өңдеудің қолдануы қарастырылған.

Кітаптарды сатып алу үшін «Қазақ университеті» баспа үйінің кітап дүкеніне хабарласу керек. Байланыс тел.: 8 (727) 221-16-07. E-mail: **baspa@kaznu.kz,** сайт: **www.magkaznu.com**.