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New Approaches to Practical High-Effective Solar Energy Conversion

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Additional information is available at the end of the chapter

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1. Introduction

High-effective solar energy conversion is impossible without deep examination of solar cell components as physical materials. Studies of structure of matter, its optical and thermodynamic properties belong to the scope of several disciplines. The concept of generalized formula units is of particular importance. For example, a category of crystal lattice is the result of crystal's mathematical modeling, while the regularity of the crystal structure represents the basis of its zone structure, which, in turn, is the model for description of energy states of the electrons. It is clear that after all chemical bonds are broken and crystal is evaporated there will be no crystal lattice and its inherent energy bands. Only particles of the crystal remain. However, the band theory considers only energy states of the electrons. Therefore, studies of the relations between structural, thermodynamic and optical properties of material without addressing to the band theory of solids are of both theoretical and practical interest. Here we show that such relations can be found by presenting the sequence of ground and excited states of primitive and non-primitive crystal cells as a thermodynamic process. Calculation of frequencies at which maximal useful work can be produced by a crystal cell and radiation is presented by the example of magnesium. The number of such frequencies increases in the row diamond-graphite-soot. On the example of silicon it is suggested that objects can be comparable with ideal radiator, or black body, in terms of their property to absorb radiation energy if they are composed of nanoparticles, i.e. clusters with small number of atoms. Requirements formulated for such objects are to be used for maximally efficient conversion of solar radiation into useful work. At the same time, current-voltage characteristics of solar cells are of special interest. We report experimental results and data of their numerical simulation showing novel features of common silicon-based solar cells with metallic Cu/Ag-nanoclustered contacts.

2. Structural and formula units of crystalline substance

2.1. History of the problem

Atomic-molecular theory of matter structure is a basis of our understanding various properties of substances. Laws of Kirchhoff, Wien, Stefan-Boltzmann and the Planck formula build a simplest model of optical, structural, thermal and chemical characteristics of substances: these laws are valid for any solids, liquids, gases, plasmas and radiation in the state of absolute black body. Our interest is focused on unity of these properties as a tool for introducing Formula Units or preventing a movement of solids to the state of black body.

This chapter presents a crystal-chemical model of unity of structural and optical properties and chemical and thermal characteristics for real solids. Self-consistence of their actions causes various departures of solid from the black body. Knowledge of these departures is necessary for proper choice of the object of investigation and working body under solving science-technological tasks, in particular, for predicting and calculating efficiency of transformation solar heat → useful work.

The simplest Kirchhoff-Planck model gives identity of the optical properties of solids. Otherwise, the optical properties of real solids may belong to two groups according to sensing their atomic structure. Structural sensitivity of optical properties depends on atomic structure of the solid; absence of this sensitivity depends principally on electronic structure of the atom, ion, and other atomic particles. The fundamental absorption of UV-radiation is an example for the first case. The own color of solids and absorption of visual and IR-radiation are an example for the second case.

The first set of optical properties is defined by chemical composition of the light absorber; the second one is defined by mechanism of interaction between light and matter. A number of original works and reference editions summarize data on optical properties of solids in various aggregate and structural states. Here we will use one of them [30, 31, 56, 61].

Thermal properties of solids are characterized by melting heat, evaporation heat, sublimation heat, and by the energy of decaying chemical bonds. They are not so sensible to atomic structure as the optical properties. Sensing optical properties to structural changes is negligible in some cases.

Thermal and chemical properties of substances are subjected to the thermo-chemistry examinations. They are defined by the laws of thermodynamics and are studied well enough. Numerous data are reported in many reference books, for example, in [70]. Correlations of thermal and chemical properties of substances are considered in chemical thermodynamics. We should note the general theory of comparative calculating thermal properties proposed by Karapetjanz M.Ch. and Kireev V.A. in [37].

Crystals are presenting the limit case of regular and periodic locations of atomic particles in space. In non-crystalline solids there are micro-and nano-parts where the regular (partially periodical or completely crystal-like) distribution of atomic particles is also realized. Thus we

will below consider the crystal as an ideal case of regular and periodical location of atomic particles.

After finding chemical individuality the crystal becomes a formula unit. The formula unit (FU) is identical to the molecular unit of the substance in symbols of chemical elements. In a period for the X-ray analysis the mineralogy had a false opinion that the minerals are built from molecules, therefore, the mathematical crystallography did not need separating categories "structural unit of the crystal" and "formula unit of the crystal". Fedorov's crystallographic analysis made it possible to define the type of crystal lattice and, using his tables of mutual arrangement of the crystal facets gave a possibility to find out the chemical composition of the mineral, i.e. the formula unit [1]. However, the Fedorov's crystal-chemical analysis did not allow determining the particles which are to be located in the sites of the crystal lattice.

Invention of X-ray analysis made it possible to highlight the formula unit from the set of many structural units of the crystal. The modern crystallography and crystal chemistry consider atoms, ions, and their groups located at the sites of the crystal lattice as structural units. The contemporary X-ray structural analysis revealed a great number of structural units of the crystal which build a hierarchy. These data are described in various publications.

We have to note here that the first separation of categories "structural unit" and "formula unit" took place not in mineralogy, but in molecular theory worked out by Avogadro. It was appeared as a tool for describing chemical interaction of gases. At beginning of 50th years of 19th century it was further developed by A. M. Butlerov in theories of chemical structure, valence and coordination compounds. At the same time Kirchhoff investigations led to optical identification of structural units of the substance-to the atom and molecule.

Spectral analysis is not a decisive tool for determining structural unit and formula unit of the crystal. For example, in the crystal of magnium oxide (periclas) one can differ atoms' groups Mg , O , Mg_4O_4 , MgO_6 , Mg_6O , and many others. The first two ones are filling in the primitive crystal cell. The third structural unit symbolizes a formula unit of the substance; the next ones present the content of the elementary cell and coordination groups of atoms. All these units are the most important parts of crystal structure of periclas. Optical identification of the crystal does not consider its formula unit as one of the structural units. Modern hierarchy of these categories had been formed in crystallography and mineralogy as a consequence of neutron, electron, X-ray, and other structural analytical methods only.

Laue M., Friedrich W. and Knipping P. in 1913 made it possible to find out a function between experimentally observed diffraction patterns from dark points at one side and real locations of atoms in crystals and X-ray wave length from the other side. Scientific achievements of Bragg W. G. and Bragg W. L. reduced the analysis of simple crystals to the standard technique. It was a beginning of a new method of crystallographic analysis called X-ray crystallography. Laue M., Bragg W. G. and Bragg W. L. were awarded by Nobel Preis (1914, 1915).

Fedorov E.S. understood for the first time that only the atoms but not molecules are to be located periodically in the space at the sites of crystal lattice [17]. It was his explanation of false attempting to connect the molecule geometry with the form of crystal [16]. Further Fedorov E. S. carefully analyzed and discussed [18] works of Bragg W. G. and Bragg W. L. [11] and had

found out that in chemical sense inorganic crystals are not built from separate atomic groups [18], he has correctly assumed existence of molecules in crystals of organic compounds [118].

[23, 36, 71] showed that the crystal structure is determined not only by the energy of particles interaction, relationship of their dimensions, polarization, but also by their number. So that the choice and numbering structural units of the crystal are of special importance for describing correlations between optical and thermal properties of crystal in dependence on the atomic structure.

X-ray structural analysis of simple crystals and complex chemically crystals allowed finding out geometric parameters of elementary cell, i.e. there is a cell of minimal dimension which keeps symmetry of atomic structure of the crystal. The relation between the volume of the structure cell V_{cell} and density of crystal ρ is as follows:

$$V_{\text{cell}} = M_0 Z / (\rho N_A),$$

where M_0 is mass of one mole of molecules, and N_A is the Avogadro constant. Letter Z denotes a number of formula units in the cell of the crystal. After substituting a picknometry density of the crystal in this relation it became clear that the parameter Z is a rational constant of the crystal structure and elemental cells of various crystals can have one, two, three, or more formula units.

2.2. State-of-the-art of the problem

In this chapter the formula unit of the crystal is a group of atomic particles corresponding to the molecule of the substance. The formula unit gives information about chemical elements and their relationship in the crystal. Thus writing the formula unit of the crystal as a set of chemical elements' symbols coincides with an analogical denote of chemical molecule. In crystal of organic compounds the formula unit of the crystal corresponds to the molecule, but its elemental cell may be formed by different molecules. The formula unit of the inorganic crystal may correspond to the real object, namely, to the molecule of substance, but its elemental cell can also not correspond to the formula unit or molecule of the substance.

Despite the evidences of ionic structure of minerals they were further called "molecules". Thus, the crystal was called "a giant molecule" [21], p.128, which is not correct. In 50th years of XX century the international crystal-chemistry literature started using the category "formula unit" as an alternative to the category "molecule". Authors [7] have critically analyzed the situation. At present time the category "formula unit" is practically usable in crystal-chemistry literature regardless the absence of its official formulation.

A long discussion how is the ionic crystal to be presented: single macromolecule or a set of any structural units was ended by separation of categories "formula unit, cell, individuum, and crystal habitus" and establishment of hierarchical relationships between them.

If using categories "formula unit" and "cell of the crystal structure" is now doubtless, the category "individual of crystal" is still attractive for researchers. This topic is almost completely

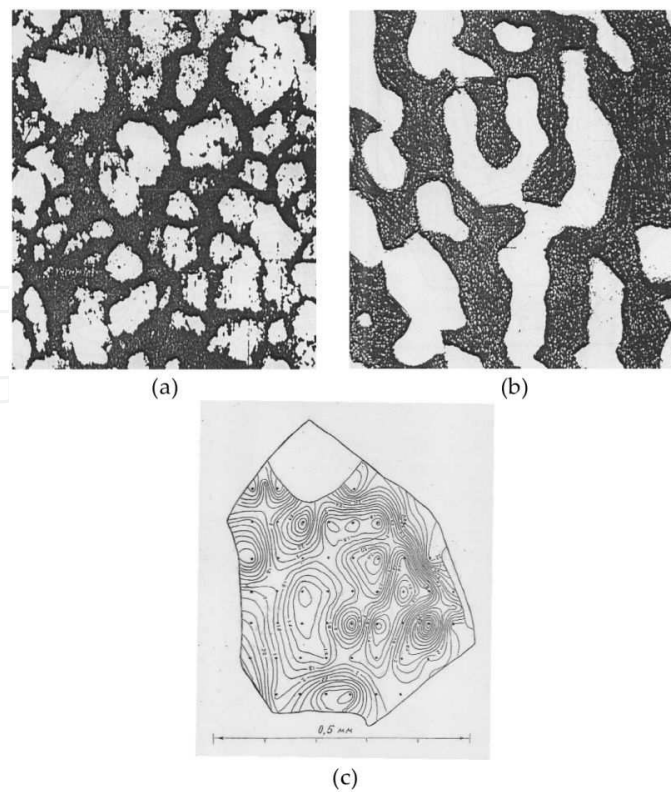


Figure 1. Cathodoluminescence image (a) of polished diamond surface (size $300 \mu\text{m}^2$) [32, 41]; auger-electron image (b) of polycrystalline lead sulphide surface [60] and the map (c) of isolines of concentration of Fe^{2+} ions in the wafer of olivine [2].

worked-out by G. B. Bokii with using an example of individuals in mineralogy [9]. Vesnin Yu. I. wrote in his preprint [73] about “elemental unit of the crystal” principally corresponding to the category of individual. At present time one considers a monograin or monocrystal with a surface of phase separation as an individual. A separate crystal block with sizes of $10^{-5} \div 10^{-6}$ cm is called sub-individual if dangle chemical bonds, linear and screw dislocation, and other defects of crystalline structure are concentrated along the boundaries of this crystalline block. These blocks are relatively disoriented in $1 - 3^\circ$, sometimes up to 5° . Namely, the sub-individuals of the crystal are regions of coherent X-ray dispersion [9].

The crystal sub-individuals may be identified by tunnel electron microscopy. Fig. 1a shows an electron image of diamond surface obtained in mode of the cathodoluminescence of the sample [32, 41]. White fields can be considered as images of sub-individuals, and the black ones are images of their boundary regions. Fig. 1b plots Auger-electron image of the polycrystalline PbS film [60]. The seed of the crystal is also may be considered as its sub-individual.

Results [2] are also present identification of olivine sub-individual by method of optical spectroscopy. Fig. 1c illustrates a map of isolines built for distribution of arbitrary concentration of Fe^{2+} ions in the wafer of olivine crystal.

The distance between the closest isolines is significantly larger than the measurement error. Points show regions of photometry. Authors [2] suppose microblock-like structure of the

olivine crystal. The blocks are of submicron sizes but they have practically same crystallographic orientation which is highlighted by simultaneous turning-off of the entire crystal in crossed Nicole prisms under microscopic examination. These properties of olivine and absence of interruptions in isolines are allowing to assume that identified blocks of the crystal are sub-individuals of olivine.

Modern X-ray analysis has no difficulties in giving principal information about geometry of crystal cells. There is a big data set on numbers and multiplicity of regular point systems, and on numbers of formula units in cells of many crystal structures. There is no doubt that these properties are affecting the facets of the crystal. Many outside forms of crystals are studied and identified. As an example one can use Fedorov's crystal-chemical analysis allowing determination of the crystal formula unit from its macro-and microsymmetry.

Habitus (facets working-out) is a visual level of structure organization of any crystal. It was found out that the facets are to be described by simple forms: by a single form or by a combination. The simple form is a set of facets defining by elements of symmetry of point group satisfying the Hauyi law. If the crystal visually outside presents the same and symmetrical facets, it can be described by a simple form. If the facets are differing by shape and size the crystal habitus may be presented by a combination of simple forms. Now we know 47 geometrically different simple forms, 146 physically different simple forms [5], and 1403 structural-crystallographic differentiations [68]. The number of facets is not countable. For example, in [23, 24] are presented more than 30000 images of the crystals.

Atoms coordination in the crystal is caused by their spatial localization. The complex of symmetry location elements does not multiply the symmetry. However, the plane out of this location will be cloned and will create one of the simple forms (shapes) depending on its placement relative to the elements of symmetry for a chosen location. When all peaks of the simple form or part of them will belong to equivalent positions relative to the chosen one, the symmetry of the simple form should be bound with symmetry of coordination polyhedron [51, 52].

2.3. The atom and nanovoid as structural units of an ideal crystal

A number of types of coordination polyhedra is limited. Creating an image of one of them reveals voids in polyhedral models of the crystal [58]. There are no sites of crystal lattice in these voids. Thus, the appearance of the voids is assumed to be explained by the category of coordination simple forms which are building the coordination polyhedron [45]. In this case the voids in polyhedral models of the crystal are explained as coordination vacancies due to partial incomplete population of peaks in coordination simple forms. From outside it can be seen as reduce of peaks in the coordination polyhedron proposed by Belov N. V. as a geometrical puzzle. In reality the coordination polyhedron is a matter image of coordination simple forms or their combinations with taking into account the population of the peaks.

It was found a mathematical relation between the number of atoms in the formula unit, coordination number of the atom, number of the facets, and the populations of peaks in simple forms [45, 46]. This relation shows that the interaction of inside structure and outside shape of the crystal is to be extended by a statement saying the following: the ideal crystal structure

there are coordination nanovoids forbidden for self-population. These nanovoids are functionally and periodically located in the crystalline structure [3, 51, 52, 65]. For example, they form well-known throughout-pipelines (channels) in diamond.

So that, the crystal has a level hierarchy of its organization as a system. The first level shows chemical composition and relationships of atomic particles. The second one presents a function of their inter-location in the space. The level presents an organization of the crystal as a physical object. Categories „ formula unit“, „cell“, and „crystal individuum“ build the basis of every level. The habitus of the crystal is supposed to be a fourth level of its structural organization.

The coordination nanovoids are to be considered as the special (zero) level of the system organization of the crystal. They reflect the fact that the empty space before its substance population is a same participant (as the atoms) in the process of crystal formation. Namely the kept primary space is built from coordination voids which may be called relic nanovoids.

The category „coordination nanovoid“ is important in other scientific fields. The nanovoids may be populated by other particles, for example, by photons, electrons, positrons, atoms or molecules. In this case the description of the particles absorber is to be started from characterizing the rest of primary space which is forbidden to the self-population by crystal substance. For example, describing the structure of periclas as a photon absorber should begin from stating the relic tetrahedral voids, and than one can highlight the atoms groups Mg, O, MgO, Mg₄O₄, MgO₆, Mg₆O and others. Further we present description of interaction between periclas and UV-radiation [49, 51, 54].

3. Amount of a substance as key category for thermodynamic and chemical description of photon absorber

The concept of "amount of substance" arose from corpuscular knowledge about the structure of matter. Dalton based his hypothesis on the number of atoms, Avogadro counted molecules. The number of substances had not differ fundamentally from the masses until the moment, when the quantum theory and the theory of relativity have shown that the mass of the atoms and molecules of the same substance in different energy states and with various total mass is not proportional to their number. For chemists, this difference of masses is minor, metrologists take it into account. The fundamental difference between the concepts of "amount of substance" and the „mass“ was relatively recently justified in Metrology. In 1971 XIV General Conference on weights and measures in its decision confirmed a fundamental difference between the mass and volume of a substance: in the International system of units was entered the seventh basic unit, which is designed to measure the amount of a substance. Its name-mol, marked with the symbol v.

3.1. Mole and kilogram: Apart and forever?

The definition is common: the mole is the amount of substance of a system which contains as many elementary entities as there are atoms in 0.012 kilogram of carbon – 12. When the mole

is used, the elementary entities must be specified and may be atoms, molecules, ions, electrons, other particles, or specified groups of such particles [33, 34]. The number of specified structural elements in one mole of a substance is called Avogadro constant (Avogadro's number), usually denoted as N_A . Thus, the carbon-12 of mass 0,012 kg contains N_A atoms. Physical value "amount of substance" should not be called a "number of moles", as it is impossible to name the physical size of the "mass" as "the number of pounds" or "number of kilograms" [12].

The current definition of the mole depends on the definition of the kilogram. The XXIV [22] adopted a resolution [22] which had proposed to re-define a mole as a category. Mol should remain a unit of amount of substance; but its value will be determined not by the fixed mass 0,012 kg of carbon-12, but by the numerical value of the Avogadro constant. On the opinion of *Bureau International des Poids et Mesures, BIPM*, «Redefining the mole so that it is linked to +an exact numerical value of the Avogadro constant N_A would have the consequence that it is no longer dependent on the definition of the kilogram even when the kilogram is defined so that it is linked to an exact numerical value of h . This would thereby emphasize the distinction between the quantities "amount of substance" and "mass"» [4].

Indeed, mass is a physical characteristic of matter, which expresses and simultaneously measures the gravitational and inertial properties of the matter. The amount of matter is the number of atoms, molecules, ions and other structural units that build the matter. One value of the mass of a substance can correspond to a series of numerical values of quantities of the substance. For example, the mass of the Universe is constant, but the amount of matter in it can be calculated differently if its structure is considered as a set of Galaxies, star systems, molecules and atoms, protons and electrons, photons or other atomic particles. The difference between mass and amount of a substance can serve as the physical basis of the existence in Nature of the right of choice. The bearer of this right is the man as a part of the Universe. The observer in the theory of relativity proofs it.

3.2. Values derived from amount and mass of substance

When building a system of units derived from number of substances the first values should be the values that are expressed only through the basic units of the system. The diagram below illustrates this requirement.

Mass, m	Amount of the substance, ν
Mole mass, $M = m / \nu$	Specific amount of substance, ν / m
Density, $\rho = m / V$?
Specific volume, $v = V / m$	Mole volume, $V_{\text{mol}} = V / \nu$

This scheme shows that its logical completion needs entering another derived value. This may be the density of the amount of substance, which is proposed to be denoted by symbol σ .

The density of substance quantity σ is a physical value equal to ratio of the amount of a substance to its volume. The equation determining σ is as follows:

$$\sigma = v / V. \quad (1)$$

According to this equation the dimension of σ is expressed by the ratio of $L^{-3} N$, where L and N are symbols of the dimension of length and amount of substance. Unit of measure for σ is "mol per cubic meter", which is in SI units equal to the density of the amount of substance, under condition: if the volume of amount of substance is one cubic meter, then the amount r of substances is one mol.

3.3. Amount of substance for some matters

Method of measuring the amount of substance is count. Direct counting atoms and molecules does not seem reasonable. Even the number of galaxies in the Universe is already not countable. For example, one of proposed models of the Universe considers it as an ideal gas, containing galaxies. Therefore, the amount of substance is calculated by measurement of volume or mass. Relations between the density of amount of substance σ with density ρ , specific volume v and molar V_{mol} volume of substance are revealed by joint solution of equations defining these values:

$$\sigma = \rho / M = 1 / vM = 1 / V_{\text{mol}} \quad (2)$$

Under calculating σ it is necessary to identify the structural element of the matter.

3.3.1. Gases

Molecule can be accepted a structural element of gas. Table 1 lists values of densities of amount of substance σ for some matters calculated according to eq. (2). Density of amount of substance for gaseous simple matters under normal conditions does not depend on chemical nature of gas and is equal 44.6 mole molecules/m³. Gas of molecules of chemical compounds has the same value of σ . The Avogadro law says that all gases in the same states have a constant value of σ . The ratio v/σ for any matters is equal to the volume of substance and does not depend on the choice of structural element.

The number of molecules determines the volume ratios of gases; the number of atoms determines weight ratios. Therefore, the density of gaseous matters has fundamentally different functional dependences: the ratio ρ / σ is equal to the mass of a mole of a substance and depends on choice of structural element, chemical nature and it is proportional to the ordinal number of the element.

3.3.2. Small particles

Atomic structure of bodies in general theory of systems supposes availability of atomic aggregates between gases and condensed bodies with properties which are fundamentally

differ or are intermediate between the properties of isolated atoms of gas and bounded atoms of bulks. Usually aggregates from two to several hundred atoms are called clusters, and the larger aggregates are called small or microparticles [13]. The clusters as well as particles can have linear size more than 1 nm. At present time they are called nano-clusters and nanoparticles that expect different dimension effects. There are no general criteria for type definition of small particles on the number of atoms. In paragraph X of this chapter we propose to consider crystalline nanoparticles the particles which have no translation in the atomic arrangement. These groups contain from 27 to 63 atoms of one chemical element, depending on the type of syngony of a bulk crystal [48, 51, 52].

It is seemed to be reasonable to identify the structural element as the formula unit in calculations of the number of substances of small particles. In the case of simple substances the mass of mole of formula units is equal to the mass of the mole of atoms; in the case of chemical compounds it is equal to the mass of the mole of molecules. Characters of these molar quantities are marked with lower index "0". Therefore, the values σ_0 may describe the density of amount of substance of nanoscaled bodies and they will be useful in examining features of dimension effects.

The principle of construction of physical quantities "density of matter and density of amount of the substance" is the same for all bodies: the ratio of the corresponding main unit to the volume as a value derived from the length. However, their functional relationships principally differ from the linear dimension. For example, the density of the bodies ρ depends on the chemical composition. The diversity of chemical composition can be expressed through the radius of the atom. In Fig. 2a these densities ρ of chemical elements are compared with the radius of the atom: any correlation between the density of small particles and the radius of the atom is not observed.

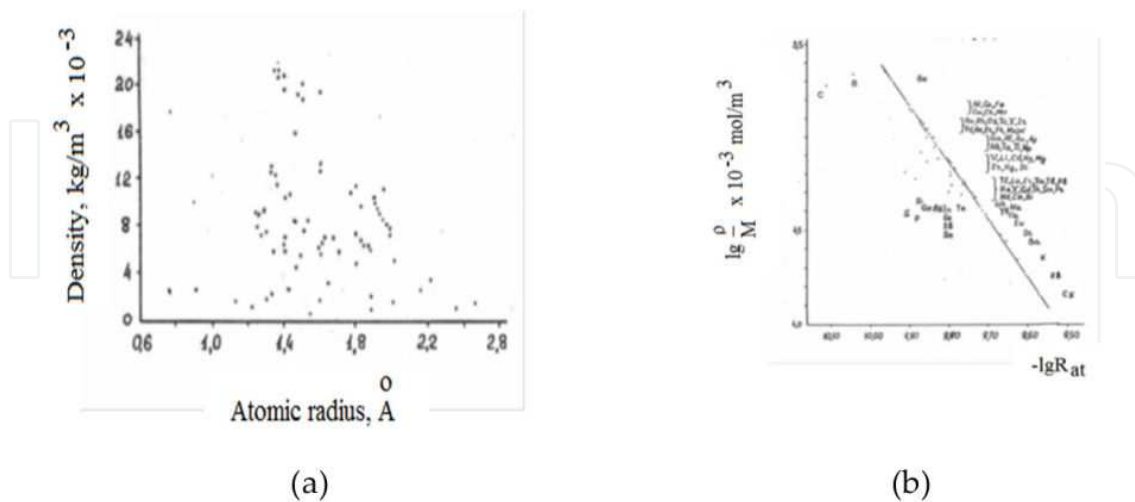


Figure 2. (a)-uncorrelative density ρ and radius of the atom in crystals of simple solids: metals, semiconductors, dielectrics. Points of gases densities are coinciding with abscissa axes; (b)-correlation between the density of amount of substance σ or ratio ρ/M_0 of the density to the mole weight and the radius of atom in simple solid. $\lg \rho/M_0=1.65$ for all gases under normal conditions.

If we take into account the chemical identity of atoms through the mass of the mole, there is a linear correlation of the amount of substance σ of the small particle from the radius of the atom. For example, the density of the amount σ of any gaseous substances under the same conditions is constant. Therefore, the boundary between the molecule, nanocluster, nanoparticle and a bulk of the given substance can be found according to the nature of the dependence of the density of amount σ_0 of the substance on the radius of atom or molecule. Let's consider a simple example.

The sizes of the atoms are in a periodic dependence on the number of the chemical element in the Periodic system. The density of amount σ_0 of gaseous substance does not depend on the size of atom or molecule. For example, for all gases under normal conditions $\lg\sigma_0$ is equal to 1.65. If $\lg\sigma_0$ of the gaseous system exceeds this value, one should consider a body consisting of small particles. The more $\lg\sigma_0$ differs from 1.65, the smaller particle differs from the molecule. Molecular associates in gases can be an example. The density of small particles in aerosols and gels is higher; the deviation $\lg\sigma_0$ from 1.65 will be significant.

3.3.3. Amorphous and dispersive bodies

In extreme cases of aggregation of atoms or molecules the density of small particle can reach the density of solid phase, in particular, of the crystalline phase. When the aggregation of atoms is completed by formation of micro-particles, the formation of a massive body is possible, and Fig. 2a can be considered as an illustration of the mass distribution in amorphous body, which represents the fine system of ultramicroparticles. Chaotic arrangement of points disappears if the value of density of substance in each point of Fig. 2a will be divided by the mass of one mole of atoms. The result is presented in Fig. 2b.

The ordinate in Fig. 2b represents the logarithm of the density of amount of substance, expressed per mole of molecules/m³. It is seen that the lowest values of σ have alkaline and alkaline-earth metals; the highest values σ have boron, beryllium and carbon. Other solid substances have intermediate values of the density of amount of substance under specification of their structural elements as formula unit.

The dependence p/M_0-R_{at} for gases can be shown in Fig. 2b by the horizontal line $\lg p/M_0=1.65$. Points between straight lines for gases and solids can be characterized the structure of small particles: from molecules, nano, nano-particles, small particle to microparticle, bulk liquid and solid body. Table 1 shows values of the density of amount σ for number of simple substances calculated by equation (2). Under calculating σ the structural element of the substance has corresponded to the chemical formula of the compound. In condensed phases the structural element in exceptional cases corresponds to a molecule or atom. The data show that the lowest values of σ have alkaline and alkaline-earth metals; the highest values of σ have boron, beryllium and carbon. It should be noted that the liquid hydrogen has maximum σ . Other solid and liquid substances have intermediate values of the density of the amount of substance under specification of their structural elements as formula unit.

substance	Atom radius R_{at}		Density of the amount of substance σ_0	Density of substance ρ ,
	10^{-10} m	$-\lg R_{at}$	or mole mass M_0 , 10^3 kg/mol	kg/ m^3
H ₂ , gas	2.22 / 1.1	9.654 / 9.559	2,0158	0,08987
H ₂ , liq.	0.3707	10.43	2,0158	708*
He, gas	1.82	9.740	4,0026	0,1785
He, liq.	0.53	10.276	4,0026	126*
N ₂ , gas	3.22 / 1.5	9.492 / 9.824	28,0134	1,2506
N ₂ , liq.	0.547	10.262	28,0134	808
Li	1.520	9.823	6,94	534
Cs	2.655	9.576	132,91	1900
Mg	1.599	9.796	24,31	1740
Ba	2.174	9.663	137,34	3760
Al	1.432	9.844	26,98	2699
W	1.371	9.863	183,85	19320
Hg, liq.	1.503	9.823	200,59	13600
Br ₂ , liq.	1.1415	9.943	159,81	3102
B	0.795	10.10	10,81	2340
Be	1.113	9.953	9,01	1850
C	0.771	10.11	12,01	1880

*Density of substance at boiling point.

Table 1. Values of density and density of amount of substance for some simple matters

According to Fig. 2b and Table 1, the points showing the density of amount of substance of liquids and radii of the atoms are arranged between straight lines for solids and gases. The position of these points allows giving a qualitative characteristic of the structure bodies. So that, liquid bromine and liquid mercury with their structure are similar to solids. In opposite, liquid helium and liquid nitrogen are maximally removed from the line of correlation. Absence of own correlation among them confirms the fact that liquids are the transitional state in condensation of gas to solid. Therefore, one should not expect the existence of a universal equation of state for liquids. These states should be described by special solutions of the equation of state of the real gas and solid body. An example is the equation of van der Waals describing condensation of gas to liquid, and a chain of equations by Bogoliubov-Born-Green-Kirkwood-Yvon (BBGKY) which describes the melting of a solid body.

3.3.4. Crystals Amorphous and dispersive bodies

The radii of atoms can be associated with periods of their location in the crystal space. In Table 2, for example, the cubic lattice provides relationships between the lattice period a and radius of atoms in the dense packing, number Z of atoms in the elemental cell of the crystal.

Lattice type	Atomic radius	Coordination number	Dense packing	Number of atoms in the elemental cell of the crystal
Primitive	$a/2$	6	0.52	1
Volume-centered	$(a\sqrt{3})/4$	8	0.68	2
Face-centered	$(a\sqrt{2})/2$	12	0.74	4

Table 2. Correlation between atoms of the dense packing with parameters of cubic lattices.

There are other relationships for crystals of another syngonies. So that, there is a possibility to move from the dependence of density ρ to the density of the amount of substance σ as a function of the volume of elemental cell of the crystal V_{cell} and number Z of formula units of substance in the cell.

The upper part of Fig. 3 presents points linking based (picknometry) density ρ and volume V_{cell} of elemental cells of the crystal determined from x-ray structural analysis data. Each point corresponds to the crystal of certain chemical composition. Chaotic arrangement of points gives place of their correlation, if the density of the crystal will be divided by the mass of the mole of formula units. It is shown in the middle part of Fig. 3. The ratio ρ/M_0 is the density of a standard amount of substance σ_0 or density of standard amount of crystal substance. It was calculated by the formula (1)

$$\sigma_0 = \rho / M_0.$$

If chemical identity of the crystal was registered by the mass of mole of formula units M_0 , the structural identity of the crystal can be taken into account by the number Z of formula units of the substance in the cell of the crystal. Lower part of Fig. 3 shows a linear correlation between the volume of the unit cell and the density of amount of crystalline substance $\sigma = \rho / (Z M_0)$. It corresponds to the formula

$$V_{\text{cell}} = M_0 Z / (\rho N_A),$$

which is known in X-ray structural analysis for calculating Z . The join solution is

$$\sigma = 1 / (V_{\text{cell}} N_A),$$

showing that the tangent of the slope of the straight line is numerically equal to the reverse value of the Avogadro number N_A .

Note some features of gradual transition from the density of the crystal ρ to its relation to molecular weight M_0 and density of amount of crystalline substance $\sigma = \rho / (Z M_0)$.

First, in Fig. 3 the properties correlation (or absence of it) completes within the error of measurement of density of substance about 400 chemical compounds of different classes.

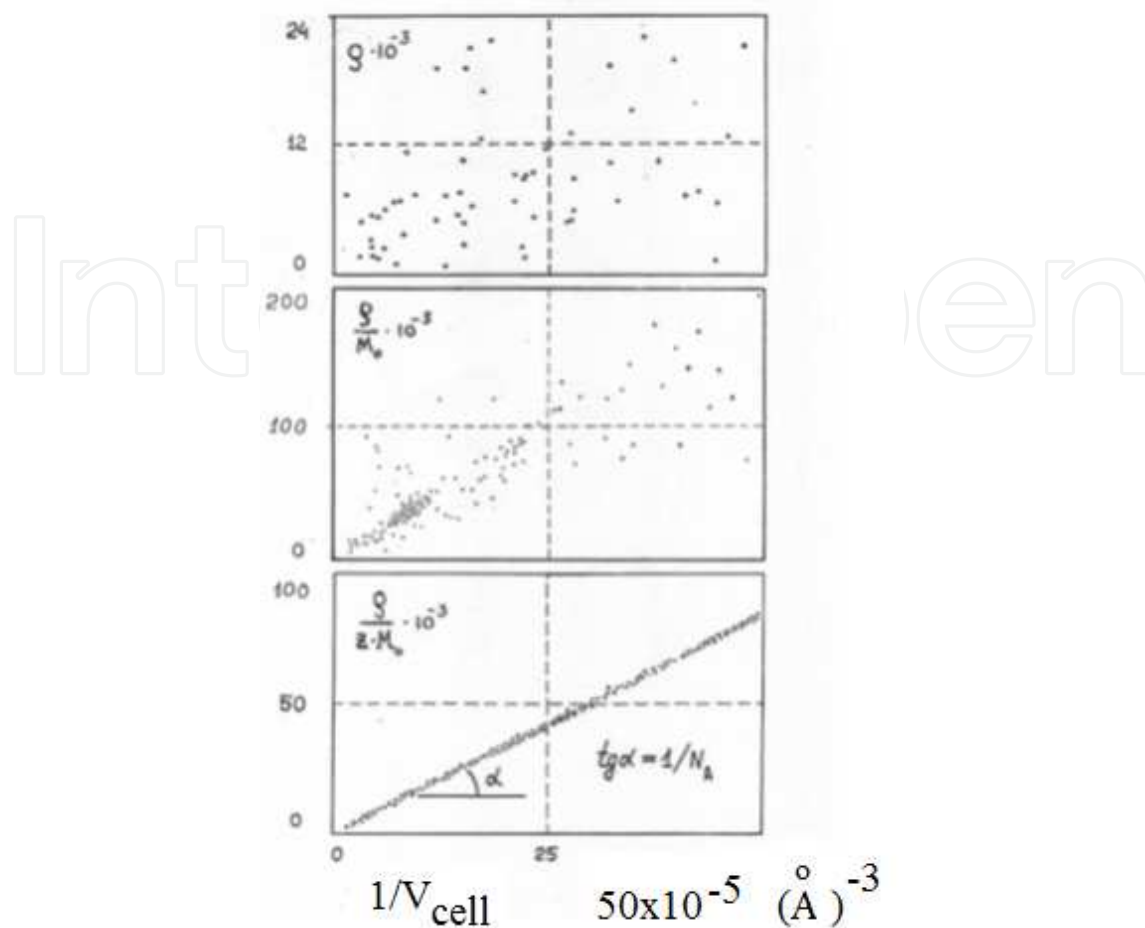


Figure 3. Evolution of correlation between the volume of unit cell of the crystal in series of properties „density – mole mass – number of formula units in the cell of the crystal“.

Electrical properties present here conductors, semiconductors and dielectrics. Chemical composition except for simple substances presents here oxides, halides, chalcogenides, oxidocompounds, nitrates, nitrites, sulphates, carbonates, iodates, bromates, chlorates, wolframites, carbides, nitrides, hydrides, hydroxides and other chemical compounds. Optical properties present here transparent and colored crystals, as well as metals. On structural properties here are the crystals of all systems (syngonies). By type of chemical bond here are presented crystals with metallic, ionic and covalent bond, and molecular crystals.

Second, the density of amount of substance $\sigma = \rho / (Z M_0)$ and the volume of the elementary cell was calculated from the experimental data. We used tables of molecular weights of chemical compounds that are defined with sufficient precision, tables of densities found by picknometry method, the cell sizes of the crystals were determined by X-ray structural analysis of crystals.

Third, the tangent of the slope of a line is numerically equal to the inverse value of Avogadro's number N_A . This result obtained in 1997 [43, 44, 51, 52] corresponds to the Resolution XXIV of the General conference on weights and measures (General Conference on Weights and

Measures, 2011), which proposed in the future to determine mol by fixation of the numerical value of the Avogadro constant.

These features allow stating that following expressions for calculation

$$\sigma_0 = \rho / M_0,$$

$$v_{m0} = (M_0)^{-1},$$

and the standard density of amount of substance of crystalline σ_0 as well as its specific amount $v_{m,0}$ are corresponding each other (Table 3).

Natural or artificial crystal	Density of mass ρ , kg/m ³	Specific density of standard amount of substance v_{m0} , mole/kg
Cu	8950	15,74
NaCl	2170	17,11
CsCl	3980	5.940
Diamond C	3470*	83,26
Lonsdeylite C	3510	83,26
Double-layer α -graphite (C-2H)	2090*	83,26
Three-layer β -graphite (C-3R)	2090*	83,26
Wurtzite ZnS	4087	10,26
Sphalerite ZnS	4090	10,26
CdJ ₂	5670	2,731

* The lowest density of natural diamonds and carbons (graphite)

Table 3. Density of standard amount of substance for some chemical elements and compounds.

Opposite, the calculation expressions

$$\sigma = \rho / (Z M_0),$$

$$v_m = v / m = (Z M_0)^{-1}$$

correspond to the density σ of real amount of crystal substances and its specific amount v_m . Table 4 shows comparison of the calculation results σ and v_m of diamonds, graphite, copper, and other compounds. These crystals are found in nature, and they are grown artificially.

One can see from Tables 3, 4 that specific amount of crystal substances of four carbon structures varies, although one kg of each allotropic form of carbon contains an equal number of atoms. However, a unit mass of a diamond and lonsdeylite, two-layer α -graphite (2H) and three-layer

β -graphite (3R) has a different number of cells. Therefore, the change in the amount of crystalline substances illustrates kinetic difference in polymorphic transformations of carbon (Table 5).

Natural or artificial crystal	Density of mass ρ , kg/m ³	Z	density of amount of crystalline substance	
			Specific density v_{m0} , mole/kg	Volume density σ , mole/m ³
Cu	8950	4	3.935	35220
NaCl	2170	4	4.278	9280
CsCl	3980	1	5.940	26640
Diamond C	3470*	8	10.41	36110
Lonsdeylite C	3510	4	20.82	73050
Bilayer α -graphite (C-2H)	2090*	4	20.82	43500
Trilayer β -graphite (C-3R)	2090*	6	13.88	29000
Wurtzite ZnS	4087	2	5.132	20970
Sphalerite ZnS	4090	4	2,566	10490
CdJ ₂	5670	1	2.730	15480

* The lowest density of natural diamonds and graphite

Table 4. Density of amount of crystalline substance of some chemical elements and compounds

Traditional form of writing phase transition	Change Δv_0 of standard amount of substance, mole	Crystal-chemical form of writing phase transition (short)	Change Δv of amount of crystalline substance, mole
Diamond \rightarrow α -graphite 2H	0	$C_8 \rightarrow 2 C_4$	2
Diamond \rightarrow β -graphite 3R	0	$3 C_8 \rightarrow 4 C_6$	1
Diamond \rightarrow lonsdeylite	0	$C_8 \rightarrow 2 C_4$	2
β -graphite \rightarrow α -graphite	0	$2C_6 \rightarrow 3C_4$	1
Diamond \rightarrow C_{gas}	0	$C_8 \rightarrow 8 C_{gas}$	8
α -graphite \rightarrow C_{gas}	0	$C_4 \rightarrow 4 C_{gas}$	4
β -graphite \rightarrow C_{gas}	0	$C_6 \rightarrow 6 C_{gas}$	6
Lonsdeylite \rightarrow C_{gas}	0	$C_4 \rightarrow 4 C_{gas}$	4

Table 5. Balance of amounts of standard and crystalline substances in polymorphic transformations and sublimation of carbon.

Crystal-chemical formulation of phase transitions of graphite is given in Table 5 in short form. It does not reflect the difference in structures of α -graphite and lonsdeylite if writing them as the form C_4 . The full form takes into account the number of regular systems of points (the equivalent of locations) in the crystal structures of carbon. So, in 2H cell of double-layer α -graphite four atoms are located at the points of two regular systems. In 3R cell of β -graphite six carbon atoms are arranged on two points of regular systems. Full form of polymorphic transformations in graphite is given in Table 6. Atoms of diamond and lonsdeylite are located on the same system of equivalent points. Therefore, the forms of their entries are given in Tables 5, 6.

Traditional and full crystal-chemical forms of writing phase transitions		Change of specific density of standard amount of substance Δv_{m0} , mole/kg	Change of specific density of amount of crystalline substance Δv_{mv} , mole/kg	Increase of amount of crystalline substance per phase transition, mole/0.012 kg
Diamond \rightarrow α -graphite 2H	$C_8 \rightarrow 2 C_2C_2$	0	10.41	1/8
Diamond \rightarrow β -graphite 3R	$3 C_8 \rightarrow 4 C_3C_3$	0	3.47	1/24
Diamond \rightarrow lonsdeylite	$C_8 \rightarrow 2 C_4$	0	10.41	1/8
β -graphite \rightarrow α -graphite	$2 C_3C_3 \rightarrow 3 C_2C_2$	0	6.94	1/12
Diamond \rightarrow C_{gas}	$C_8 \rightarrow 8 C_{gas}$	0	72.9	7/8
α -graphite \rightarrow C_{gas}	$C_2C_2 \rightarrow 4 C_{gas}$	0	62.5	3/4
β -graphite \rightarrow C_{gas}	$C_3C \rightarrow 6 C_{gas}$	0	69.4	5/6
Lonsdeylite \rightarrow C_{gas}	$C_4 \rightarrow 4 C_{gas}$	0	62.5	3/4

Table 6. Change of specific amounts of standard and crystalline substance under polymorphic transformations and sublimation of carbon

Suppose that 0.012 kg of α -graphite 3R turn on the β -graphite 2H. The initial amount of crystalline substances is 1/6 mole, as $Z=6$, and in 3R cell of β -graphite six carbon atoms are arranged on points of two regular systems. The amount of crystalline substance obtained from the phase transition 3R \rightarrow 2H, will be 1/4 mole, because $Z=4$, and in 2H cell of α -graphite four atoms are located at the points of two regular systems. So, 0.012 kg of graphite from a form 3R turns into 2H with decrease of crystalline substance 1/4-1/6=1/12 mole. The increase in the amount of crystalline substance for other phase transitions is shown in Table 6.

Suppose now that 0.012 kg of diamond turned into Lonsdeylite. The initial amount of crystalline substances is 1/8 mole, as $Z=8$, and eight carbon atoms are arranged by points of one regular system. The amount of crystalline substance obtained for the phase transition diamond \rightarrow lonsdeylite will be 1/8 mole, because four atoms in the cell of lonsdeylite are located on the points of one regular system. Table 5 shows the changes in the amount of crystalline substances in all possible polymorphic transformations of diamond and graphite.

3.3.5. Crystal twinnings

Natural graphite is a cluster of two modifications of carbon 2H and 3R: the content of rhombohedral modifications may reach 30%. Therefore, calculating the specific amount of crystalline substance

$$v_m = v / m$$

of the whole crystal requires knowledge of the part of one of the structures. If the part of two-layer packaging of graphite is equal to x , then its mass will be equal xm , and the weight of three-layer packaging of graphite shall be equal to $(1-x)m$, where m is the mass of the entire crystal. The number n of all cells of graphite is

$$n = N_A [xm / 4M_0 + (1-x)m / 6M_0],$$

where $M_0 = 0.012$ kg/mol. We denote the ratio mN_A / M_0 by symbol n_0 . Then the ratio $n_0 / n = \beta$ will express the ratio of the number of carbon atoms to the number of all cells of the crystal, and the equation written above can be reduced to $\beta = 12 / (2+x)$.

The value of x for mechanical mixtures of pure graphite 2H and 3R is determined by weighing components. If case of clusterization it is necessary to calculate β with knowledge of x which can be determined by the spectrophotometric method, comparing the absorption intensity of UV radiation at wavelengths 219\AA and 418\AA , the principle of which is described below in the section 6.1. If intensities of these peaks of absorption of UV-radiation in Fig. 8 identified by the symbol h , then the value of x can be calculated from the equation

$$h_1 / h_2 = x / (1 - x)$$

Having determined the value of x from the spectral experiment, one can calculate the specific amount of crystalline substance in the cluster of graphite by the formula

$$v_m = v / m = (\beta M_0)^{-1}$$

and density of crystalline substance of graphite by the expression

$$\sigma = v / V = \rho (\beta M_0)^{-1},$$

where ρ is the density of graphite. Let in Fig. 8 $x = 0.8$. Then the value β of is $12 / (0.8+2) = 4.29$, and specific quantity of crystal substance of crystal is $1 / (4.29 \times 0.012) = 19.44$ mol/kg. If the density of graphite is taken to be equal 2090 kg/m³, then the desired density of the amount of crystalline substance which is to be found for the graphite cluster will be $19,44 \times 2090 = 40640$ mol/m³.

3.3.6. Solid solutions

Mixtures are homogeneous, uniform, multi-component systems that have no separation surface between any parts. The properties of all the parts of such systems are the same. So we can assume that the structural element of the substance of the solution of given composition is the same throughout the volume of solution. Properties of solutions are a function of composition. Consider one of these functions for two cases of specification of the structural elements: formula unit and their number Z in the unit cell of the crystal.

According to formula (2), for one mole of amount of crystalline substance of solid solutions equality is valid:

$$\rho / M = 1 / (v N_A), \quad (3)$$

where ρ is the density of a substance, M is the mass of one mole of a structural element of substance of solid solution, v is a volume of a structural element, N_A is the Avogadro constant. The mass M of the mole of structural elements will be expressed through mass M_0 of mole of formula units of solid solution, and the value of Z which is the number of formula units in structural cell of crystalline material:

$$M = Z M_0 \quad (4)$$

The mass of mole of formula units we express by the sum

$$M_0 = \sum M_i N_i, \quad (5)$$

where M_i is a mass of mole of formula unit of i -component of the solution, and N_i is its mole part. Multiply the left and right parts of the solution of equations (3)-(5) by the multiplier $M_i N_i$. We get ratio

$$Z M_i N_i / (\rho v N_A) = M_i N_i / \sum M_i N_i. \quad (6)$$

We denote the left part of this ratio as H/N_A and the right part we denote by k symbol. The value of k is a dimensionless and it corresponds to the fraction of total mass by way of expression of the concentration of a solution. Therefore, the value of H has the same dimensionality [the number of particles/mol] that the Avogadro constant. For i -component of the solution we obtain the expression

$$H_i = k_i N_A. \quad (7)$$

Experimentally determined values of p , v , Z and M_{0i} building the amount H_i , are connected with it by a linear dependence with mass fraction k_i of i -component of solid solution. The relation (7) is interesting because empirical rules of L. Vegard and Rutgers are particular cases of demonstration of the function found above according to (7).

Indeed, L. Wegard had found out an additivity of sizes for the elementary cell of solid solution:

$$a = N_1 a_1 + N_2 a_2,$$

where N_1 and N_2 are the molar fractions, a_1 and a_2 are any parameters of a cell of pure components or any average interatomic distance. Additivity of the cell volumes is set by the rule of Rutgers, which is written as

$$V = N_1 V_1 + N_2 V_2,$$

where V , V_1 and V_2 are the molar volumes of solid solution and pure components. However, there are quite common deviations from these rules. Examples are solid solutions of NaCl-KCl [71]. Deviations from the rules of L. Vegard and Rutgers can have alternating nature. An example is solid solution Ni-Al.

It should be noted that the additivity of the parameters of a cell does not mean additivity of the cell volume. The equality (6) allows avoiding this contradiction and using parameters and the volume of the cell of the crystal as an example of simple linear function (7) in systems with deviations from the rules of Vegard and Rutgers.

Dependences of lattice constants and densities of solid solution Ni-Al on the structure are presented in Fig. 4a [38]. Solid solutions Ni-Al crystallize in the structural type of cesium chloride and have region of homogeneity between 45 and 60 at.% nickel. The curve of dependence of the lattice parameter on the composition has a maximum, and density curve has a sharp bend. Such curves indicate that in the region of low concentrations of Nickel we have solid solutions of subtraction: the structure has defects, and a part of places for Nickel atoms remain empty. These voids are statistically distributed throughout the volume of the crystal. Solutions with a Nickel content of more than 50 at.% are normal solutions of substitution, in which the atoms of Nickel are statistically replaced by atoms of aluminium.

Let us transform the diagram "property-structure" in Fig. 4a in the diagram "H-k" of solid solutions Ni-Al as an illustration of the function (7). To do this, we calculate the values of H and k for Nickel. The symbols characterizing its properties will be denoted with footnote index 1. Solid solutions Ni-Al have a cubic cell with a parameter a . Therefore, the volume of their structural element is equal to a^3 . Then

$$\begin{aligned} H_1 &= Z M_1 N_1 / (\rho a^3), \\ H_2 &= Z M_2 N_2 / (\rho a^3), \\ H_1 / H_2 &= M_1 N_1 / (M_2 N_2) \end{aligned} \quad (8)$$

The value of the Z of solid solutions of substitution is equal to 2 (body-centered cube), and for solutions of subtraction Z is less than two, even though the cell structure is also a body-centered

cub. Assume Z equal to $4N_1$, as at $N_1=0.5$ solid solutions of subtraction become normal solid solutions of substitution with $Z=2$. Values of density of crystals ρ and lattice parameters a of solid solutions remain unchanged.

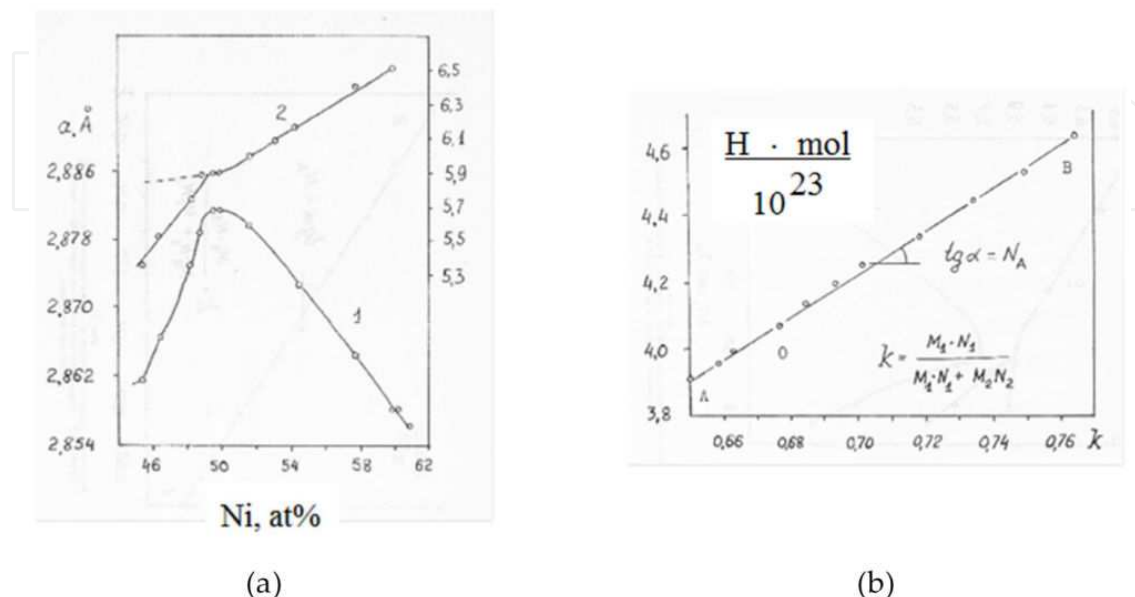


Figure 4. (a)-lattice constant (line 1) and density (line 2) for solid solutions Ni – Al as functions of Ni concentration in at.% [38]; (b)-diagram «H – k» of solid solutions Ni – Al as dependence of the value H_1 on Ni concentration in mass parts of k . Straight line AO corresponds to solid solutions of subtraction, straight line OB corresponds to solid solutions of substitution.

Values k_1 of nickel were calculated according to (6) – (7) by the expression

$$k_1 = M_1 N_1 / (M_1 N_1 + M_2 N_2), \quad (9)$$

where M_2 and N_2 are the mass of mole of aluminium atoms and its molar fraction in solution. Calculated by formulas (8), (9) the values of k_1 , N_1 for Nickel are presented in Table 7. Fig. 4b shows a diagram “H-k” for solid solution Ni-Al, which presents the relation (7) as line AOB. Part of the line AO corresponds to solid solutions of subtraction, the section OB corresponds to solid solutions of substitution.

Now suppose that the atom as formula unit is chosen as a structural element of crystalline substance of solid solution Ni-Al. Then the amount per structural element of the substance of solid solution equals to $a^3/Z=a^3/2$ for solutions of substitution as well as for solutions of subtraction. Symbols of values related to the mole of formula units we denote by lower index 0. To show that the value of H_0 , referred to mole of formula units of crystal, has no universality of the values of H_1 found above, we divide both sides of (3) by a molar part N_1 of the component. Taking into account the relation (5)

$$M_0 = \sum M_i N_i,$$

Mole part of Ni, N_1	Mass part of Ni, k_1	Lattice parameter, $a/\text{\AA}$	Density of solution ρ , kg/m^3	Number of formula units in the cell, Z	$H_1 \text{ mol} / 10^{23}$	$H_{01} \text{ mol} / 10^{23}$
0.46	0.650	2.864	5430	1.84	3.895	2.998
0.47	0.659	2.868	5550	1.88	3.962	3.008
0.48	0.668	2.873	5700	1.92	4.002	2.998
0.49	0.676	2.880	5900	2	4.081	2.957
0.50	0.685	2.882	5920	2	4.142	3.023
0.51	0.694	2.881	5960	2	4.201	3.089
0.52	0.702	2.879	6000	2	4.264	3.158
0.54	0.719	2.875	6140	2	4.345	3.265
0.56	0.735	2.869	6250	2	4.454	3.395
0.58	0.750	2.864	6400	2	4.529	3.501
0.60	0.765	2.858	6500	2	4.642	3.639

Table 7. Structure parameters of solid solution Ni – Al [38] and values of k_i , H_1 for Ni calculated according to (8), (9).

we obtain the following expression for mole parts of Ni or Al:

$$\begin{aligned}
 H_{01} &= N_1 (M_1 N_1 + M_2 N_2) / (\rho v) = N_1 N_A, \\
 H_{02} &= N_2 (M_1 N_1 + M_2 N_2) / (\rho v) = N_2 N_A, \\
 H_{01} &= H_{02} (N_1 / N_2)
 \end{aligned}
 \tag{10}$$

Denoting left parts of equations as H_{0i} , we reduce it to a general form

$$H_{0i} = N_i N_A, \tag{11}$$

Which formally coincides with (7), but with different form of expressing the concentration: the mole fraction N instead of the mass part k , i.e.

$$H_i / H_{0i} = k_i / N_i.$$

Values H_{01} for Ni are calculated according to the expression

$$H_{01} = N_1 (M_{01} N_1 + M_{02} N_2) / (\rho a^3 / 2) = N_1 N_A, \tag{12}$$

they are presented in table. 7. Fig. 5 shows that diagram " $H_{01}-N_1$ " in region of homogeneity of solid solutions Ni-Al represents two curves instead of one curve; these two curves are broken on the border of two types of solid solution. The line has a tangent of slope angle 6×10^{23} close to the numerical value of Avogadro constant. Thus, equation (11) is valid only for the region of solid solutions of substitution with some deviation, value H_{01} of solid solutions of subtraction does not depend on the concentration.

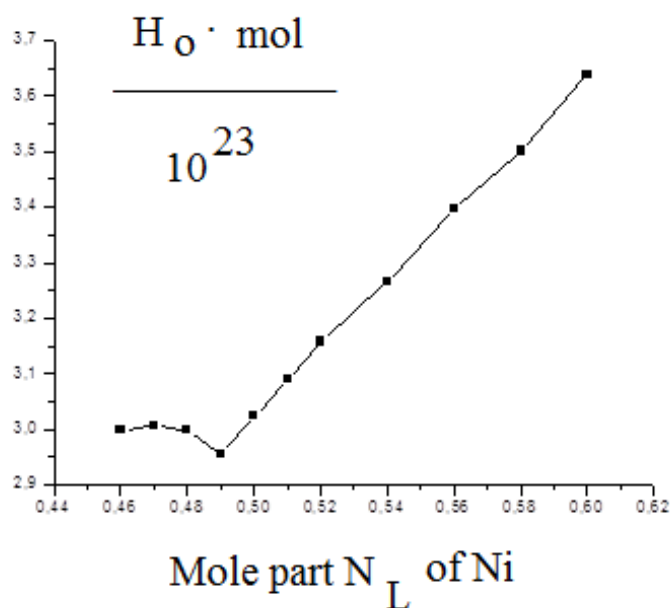


Figure 5. Dependence of the value H_0 on the mole part Ni for solid solutions Ni – Al. Horizontal line corresponds to solid solutions of subtraction, the slope line corresponds to solid solutions of substitution. Structural element of crystalline substance is specified as atom of Ni or Al.

Comparing Figs. 7, 8 and 9 shows the three representations of the experimental data on density and parameters of a crystal cell. Two of them are based on the idea of a structural element of the crystal in the form of formula unit. In this case it is an atom of Nickel or aluminium. Curves have maximum, break and other geometrical features. A third way to view ρ and a of crystals of solid solutions is based on the specification of the structural element of crystalline substance in the form of elementary cell. In this case, there is a linear function H_i of chemical composition for the whole range of homogeneity of solid solutions regardless of the type of structure and its defectiveness. Compactness, simplicity and universality of diagram presentation of the experimental data on density and the crystal unit cell parameters in dependence on mass fraction show its advantage over other methods of presentation of the concentrations of solid solutions.

The value H has dimension [the number of particles/mol]. When the mass of solid solutions remains constant, the value of H indicates a change in the number of crystalline substance of solid solutions with concentration. The range of homogeneity and cell parameters of solid solutions depend on temperature and pressure. Therefore, the amount of crystalline substance of solid solutions is also dependent on temperature and pressure.

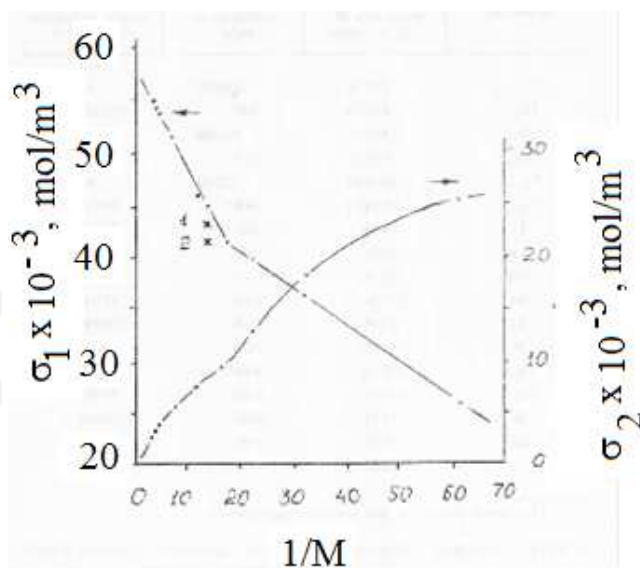


Figure 6. A change of density of amount of matter in series of liquid alkanes from methane to eicosane as a function of reciprocal mass of mole of molecules. The lower curve corresponds to the specification of the structural element of a liquid substance in the form of molecule, straight lines and points 1, 2 correspond to the specification in form of groups of hydrogen atoms with one atom of carbon.

3.3.7. Liquid alkanes

We calculate the density of a standard amount of substance in a series of liquid alkanes from methane to eicosane by the formula

$$\sigma_0 = \rho / M_0$$

where ρ is the density of the fluid, M_0 is the mass of the mole of molecules. The dependence of the density of the amount of liquid alkanes on chemical composition is presented in Fig. 6 as a function σ_0 from the reciprocal mass of mole of molecules M_0 . It is seen that σ_0 decreases in a series of alkanes from methane to eicosane, and the nonlinearity of the function is explained by the different densities of alkanes, which depends on the length of the carbon chain of the molecule and hydrogen environment of the carbon atom.

Remember that on the Butlerov's theory properties of organic compounds are sufficiently determined by the number and spatial position of carbon atoms in the chain of the molecule. So we give up on the structural element of liquid alkanes in the form of molecules and choose the structural element of a liquid substance in a series of alkanes in the form of groups of hydrogen atoms with one atom of carbon. In this case, the density of the amount of substance must be calculated by the formula

$$\sigma_n = n\rho / M_0$$

where n is the number of carbon atoms in the molecule. Function σ_{n-1} / M_0 is also presented in Fig. 6. In this case this function is linear and is explained by features of building a carbon

chain of alkanes molecules. The fracture of the line can be explained by the different amount of hydrogen associated with the given carbon atom. Indeed, among methane and butane prevails group CH₃ (bottom line), in the rest of alkanes prevails the group CH₂ (upper line). As

$$v_0/\sigma_0 = v_n/\sigma_n = V,$$

the different volumes of atomic groups explain various slope of straight lines in Fig. 6.

In a series of molecules of isoalkanes one can choose groups S, CH, CH₂ and CH₃. The value σ of normal pentane C₅H₁₂ or



corresponds to the top line in Fig. 6, as in its molecule the group CH₂ dominates. The value σ of isopentane (CH₃)₂CH₂CH belongs to the bottom line (point 1), as in its molecule the group CH₃ is predominant. The value σ of neopentane (CH₃)₄C does not belong to these lines (point 2), as in the molecule, one carbon atom is not bound with hydrogen. As pentane isomers with equal chemical composition have a different density of amount of substance, the phenomenon of isomerism is characterized not only by different geometry of molecules, but a different amount of substance. Kinetic equations of chemical reactions are determined by the number of reacting substances. Therefore, the characteristics of the reaction of pentane isomers can be described with the values of the density of the amount of substance in the kinetic equation.

3.4. Summary

The diversity of the aggregate state and structural bodies are shown in the diagrams called "state diagrams" for one-, two-, and three-component systems. Phase boundaries are depicted graphically in the coordinates of temperature and pressure, temperature and composition. We have shown above that the intersection of the phase boundaries is accompanied by changes in the amount of substance under given mass of this substance. Therefore, the authors of this Chapter argue that *the amount of substance is a function of temperature, pressure and composition*.

Presented here and previously received the knowledge of the amount of substance [42, 43, 51] corresponds to the resolution of XXIV the General conference on weights and measures, which proposes in future to link determinations of the amount and mass of the substance [22].

4. The nanovoid of an ideal crystal

This section shows that crystallographic nanovoids, which are not defects of the crystal structure, may be limited to atom filling. It is suggested that we consider coordination polyhedra as simple forms or consider their combinations. The relation between the multiplicity, the number of regular point systems, the coordination number, and the number of

formula units per unit cell is obtained in the form of algebraic equations. On the basis of these equations, it has been shown that for all 14 Bravais lattices there are 146 corresponding coordination spheres with an arrangement of atoms inside these spheres that is consistent with both space and point groups of symmetry. The shapes of the coordination polyhedra inscribed into these spheres correspond (with due regard for the vertex occupancies) to 146 crystallographic types for 47 simple forms.

4.1. Atom and Nanovoids in the polyhedron model of an ideal crystal

The idea of providing the coordination polyhedron in a crystal belongs to L. Pauling. N. V. Belov identified more complex and less symmetric forms of coordination polyhedra than the octahedron and the tetrahedron. As a further development of the polyhedron method of presentation for the crystal, one can consider the idea of the image of the coordination polyhedron combinations of simple forms [45] because through these combinations it is possible to explain the role of voids in the polyhedral models of crystal structures.

Using examples of the structures of periclase, sphalerite, wurtzite, fluorite, rutile, anatase, brookite, nickeline, barite, stannum, hydrargyrum, copper, and magnesium the following regularity is found:

- if the forms of nanovoids correspond to the class of symmetry of the crystal, they are becoming the uninhabited vertices of simple forms that construct the coordination polyhedron and the nanovoids have coordination vacancies;
- if the forms of nanovoids do not correspond to the class of symmetry of the crystal, the vertices and faces of the coordination simple form are settled and the nanovoids have no coordination vacancies.

So, the concept regarding coordination vacancies that are unpopulated vertices and the faces of coordination simple forms is formulated. Coordination vacancy may coincide with the host lattice or it can be in the interstitial space. In the first case, the filling or the formation of coordination vacancies leads ultimately to a change in the symmetry of the structure. As an example, we can look at the structural transition in the system Ni-As. In the second case, coordination vacancies can be populated with impurity atoms (diamond) or extra electrons of π -bond (graphite) and unattributed electron pairs (litharge).

4.2. Crystallochemical vacancy in the nanovoid of an ideal crystal

One of the most important properties of a crystal is the coordination of the constituent atoms. The coordination polyhedron in a crystal was isolated for the first time by [58]. Then the method of coordination polyhedra was successfully developed by [3]. The coordination of atoms in crystals was also considered in recent publications by Urusov, O'Keeffe, Parthe, and Grekov [26, 55, 57, 71]. The present study is developed toward the establishment of the relation between the number (Z) of the formula units per unit cell of the crystal and the coordination number (c.n.). As far as we know, there are no other publications addressing this particular topic.

The number Z of the formula units per unit cell of a real crystal is usually determined by the formula

$$Z = V_{\text{cell}} \rho N_A / M_0$$

where V_{cell} is the cell volume unit, ρ is the measured density, N_A is the Avogadro constant, and M_0 is the molar weight. The value of Z for an ideal crystal can also be calculated without this formula by invoking the concept of a regular point system. With this aim, we denote the total number of atoms in the unit cell with P , the number of regular point systems with n , and the multiplicity of an regular point system with k . According to the [69], we obtain the dependence of the form

$$Z = (q + 1) s (p_i)^{-1} \sum_n (1/S_i) / \sum_m (1/S_i^*). \quad (13)$$

where q is the number of additional translations equal to unity for A , B , C , and I cells. S_i is the factor that characterizes the symmetry of the position in regular point system. The symmetry factor S_i is a numerical indicator of the position symmetry that indicates the order of the point group for the special position [75]. S_i^* is the symmetry factor of the subgroup characterizing the position of a face of the particular simple form in the point group, which, in turn, characterizes the symmetry of the simple form itself. Here s is the number of the faces of several simple forms (see in detail in [45]). The characteristics of the space and point groups are borrowed from [27] and the description of the structure is borrowed from [8, 39, 59].

In particular, Eq. (13) establishes the relation between the number of the formula units in the unit cell of a crystal and the number of faces of the coordination polyhedron. The relation between the convex coordination polyhedron and the coordination number is described by the Euler-Descartes formula [39] in the following form

$$s + v = e + 2, \quad (14)$$

where s and e are the number of faces and edges of the coordination polyhedron, respectively. The number of the coordination-polyhedron vertices is denoted by v and is equal to the coordination number if all the vertices are occupied by atoms. Relationship (14) is invalid for monohedra and pinacoids that are characterized by $s=1$ and $s=2$, respectively. Their faces may have one or several regular point system positions forming various figures.

The separation of coordination polyhedra and the determination of the coordination numbers of atoms is not always unique. The simplicity and clear representation of these concepts for cubic structures is partly lost for more complicated structures with low symmetry. For more details see e.g. [8, 71]. Here, we should like to note only that the coordination polyhedra do not necessarily look like simple forms or their combinations. In this case, some vertices may be unoccupied and can be considered crystallochemical vacancies with occupancy δ . Therefore Eq. (14) takes the form

$$s + c.n. / \delta = e + 2.$$

The reduction of the coordination polyhedra to simple forms or their combinations is similar to a certain normalization procedure leading to self-consistent coordination numbers and is somewhat analogous to the representation of a crystal structure by Bravais lattices or their combinations.

4.3. The atom and nanovoid as two entities of an antenna process in a crystal

Thus, the action of the photon antenna in the crystal may be considered a reversible movement of the particle from its equilibrium position (for example, the lattice's site) into a nanovoid, and this nanovoid is forbidden from being steadily filled in by the symmetry of placement of the neighbor particles. This nanovoid pushes out the particle resulting in photon absorption in the initial position. If this cycled process is accompanied by the absorption and radiation of the photon, it may be considered an antenna process.

5. The nanovoid and predissociation of an ideal crystal cell

The sublimation, dissociation, or destruction of a crystal is the process of destroying those chemical bonds that place atomic particles in the space periodically. This section examines the crystal predissociation as a state of its particles that follows after the breaking of the chemical bonds of the crystal cell and directly precedes their scattering. A description of the crystal predissociation is missing in the literature, but it is similar to the predissociation of molecules in gas, which has been studied well enough. In this section, we consider the fragments of an ideal crystal. These fragments are restricted based on the number of atomic particles. The elemental cell of the crystal serves as an example of such a fragment.

5.1. The molecule predissociation in a void

The predissociation of molecules is a non-radiant transition of the excited molecule with a stable electronic state to an unstable one with the same energy, accompanied by the dissociation of the molecule [62]. The phenomenon of the molecule predissociation is explained on the basis of curves of potential energy. They are presented in Fig. 7a.

Under interaction with a photon, the molecule moves from the basic electron state (curve in Fig. 7a) into the excited one (curve 2); here the vibrational motion of the molecule enables the non-radiant transition to the repulsion curve (curve 3), which leads to the dissociation of the molecule. Being in the predissociation state, the molecule dissociates if its full energy exceeds the energy of separated particles that diverge along the potential curve of repulsion. Particles scatter with a kinetic energy

$$\varepsilon_{\text{kin}} = \varepsilon_{\text{pr}} - D_0 \quad (15)$$

where ε_{pr} is the predissociation energy and D_0 is the energy of molecule dissociation. In the case of a gently sloping repulsion curve, D_0 can have a smaller departure from ε_{pr} . If there is no separation then from Eq. (15) it follows that

$$\varepsilon_{\text{pr}} = D_0, \quad (16)$$

because in this case $\varepsilon_{\text{kin}}=0$. Therefore, the energy of molecule predissociation, ε_{pr} is a limit for the energy of dissociation, D_0 .

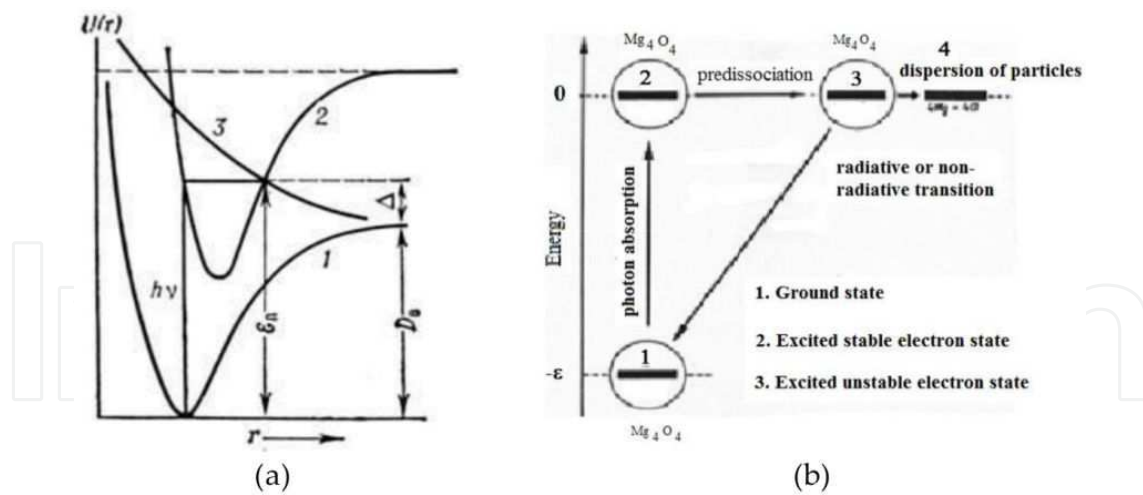


Figure 7. (a)-predissociation scheme under molecule transition to the repulsion curve: 1 and 2 are attraction curves in the basic electronic state and in the excited electronic state, respectively; 3 is the repulsion curve; ϵ_n and D_0 are energies of predissociation and dissociation, respectively; D is the kinetic energy of the scattered atoms [62]. (b)-Predissociation in the scheme of energy states in the cell of a periclase crystal after the resonance absorption of a photon with energy $Z\Delta H_{\text{subl}}/N_A$. The particles are in the sites of the crystal lattice (states 1 and 2); in state 3 the particles are displaced in the nanovoids of the crystalline structure of the crystal as a solid system.

5.2. The photopredissociation in a void of an ideal crystal

According to the Frank-Kondon principle, the transition corresponding to the crossing attraction and repulsion curves is the most probable. From (Fig. 7a) one can suppose that Eq. (17):

$$\epsilon_{\text{pr}} = \epsilon \quad (17)$$

is correct, where ϵ is the energy of the absorbed photon. Joining Eq. (16) and (17) we obtain

$$\epsilon_{\text{pr}} = D_0 = \epsilon \quad (18)$$

There are no molecules in ionic and covalent crystals, or in amorphous and liquid solids. However, we can write equations similar to Eq. (16)–(18) for the condensate state of the matter.

In laser technology, the film's solid target is under the action of a powerful radiation flux. If this power is over 10^9 W/m^2 , the sublimation of the target occurs. The expression for the kinetic energy of the i -particles can be written by analogy with Eq. (15) in this form:

$$\epsilon_{\text{kin}} = \epsilon_{\text{pr}} - f(D_{\text{subl}}, Z),$$

where ϵ_{pr} is the energy of cell predissociation consisting of Z chemical formula units, giving birth to i -particles, and D_{subl} is the energy of sublimation of a mole of chemical formula units.

When the laser radiation power is less than 10^9 W/m², a crystal melts. At still lower radiation capacities, for example, in the spectral experiment, the destruction of the crystal does not take place, i.e. the value $\varepsilon_{\text{kin}}=0$. Assume also that

$$\varepsilon = f(D_{\text{subl}}, Z, \varepsilon_{\text{pr}}),$$

describes the interaction of radiation with the solid in regards to which predissociation states may be realized.

As an example, we consider the cell of periclase (Mg_4O_4), while $Z=4$. The cell can increase its potential energy through the resonance absorption of a photon with energy ε . Then, according to Fig. 7 we can write

$$(\text{Mg}_4\text{O}_4)^0 = (\text{Mg}_4\text{O}_4)^* + \varepsilon, \quad (19)$$

where $(\text{Mg}_4\text{O}_4)^0$ is the basic state of the cell and $(\text{Mg}_4\text{O}_4)^*$ is an excited state. We can write

$$\text{Mg}_4\text{O}_4(\text{crystal}) = 4 \text{MgO}(\text{quasi-gas}) + Z\Delta H_{\text{subl}}/N_A, \quad (20)$$

Comparing Eq. (19) and (20) one can acknowledge that if the states

$$(\text{Mg}_4\text{O}_4)^0 \text{ and } \text{Mg}_4\text{O}_4(\text{crystal})$$

are energetically identical, the predissociation of the crystal cell in Fig. 7 may be presented as a transition



between energetically identical states if $\varepsilon = Z\Delta H_{\text{subl}}/N_A$.

Shown below are the particles filling the crystallographic cells; this process is accompanied by the formation of nanovoids in the space of an ideal crystal. Filling in these nanovoids can damage the cells' symmetry. If the particles can temporarily move into these nanovoids after photon absorption, we have a prerequisite for the particles' predissociation as a stage of the antenna process without any damage to the symmetry of the crystal as a whole.

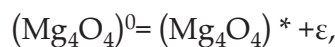
5.3. The atom and nanovoid as two entities of a crystal

The destruction of the crystal does not take place in the spectral experiment. Assume ε is the absorption photon energy, ε_{pr} is the predissociation energy and D_{subl} is the energy of crystal dissociation. If that is true, then the function

$$\varepsilon = f(D_{\text{subl}}, Z, \varepsilon_{\text{pr}}),$$

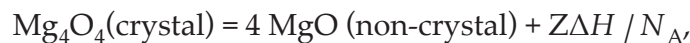
describes the interaction of radiation with the crystal where the predissociation states may be realized (see §4 in this chapter). Value Z in this function makes it possible supposing that the nanovoids between atoms of Z formula units are providing the space necessary for pre-dissociation of particles belonging to the crystal cell. Let's show a role of nanovoids in pre-dissociation of particles using an example of crystals with three different structures.

1. As an example, we consider the cell of periclase, Mg_4O_4 , while $Z=4$. The cell can increase its potential energy through the resonance absorption of a photon with energy ε . Then, according to Fig. 7b we can write



where $(\text{Mg}_4\text{O}_4)^0$ is the basic state of the cell and $(\text{Mg}_4\text{O}_4)^*$ is an excited state.

The anions of oxygen form cubic close packing [65]. There are octahedral and tetrahedral voids. All the octahedral voids are filled in with cations; all the tetrahedral voids are empty. If four tetrahedral voids are temporarily filled in due to photon excitement, the part of the solid (4MgO) will lose the particles' placement symmetry, and we will write



Comparing those states one can acknowledge that if the states



are energetically identical, the predissociation of the crystal cell in Fig. 7b may be presented as a transition of the particle into the nanovoid with the following dispersion in the crystal



between energetically identical states if $\varepsilon = 4\Delta H_{\text{subl}} / N_A$. Thus, in Mg_4O_4 cell of magnesium oxide crystal there are $2Z=8$ tetrahedral voids providing their space to 4 Mg atoms at the moment of pre-dissociation of Mg-O chemical bonds in spectral experiment.

2. As an example we consider the cell of sphalerite, Zn_4S_4 , while $Z=4$. The cell can increase its potential energy through the resonance absorption of a photon with energy ε . Then, according to Fig. 7b we can write



where $(\text{Zn}_4\text{S}_4)^0$ is the basic state of the cell and $(\text{Zn}_4\text{S}_4)^*$ is an excited state.

Sulfur anions form cubic close packing with tetrahedral voids [65]. Half of them are filled in with zinc cations, while the second half is empty. When four tetrahedral voids are temporarily filled in due to photon excitement, the part of the solid (4ZnS) will lose the particles' placement symmetry, and we will write

$$\text{Zn}_4\text{S}_4 (\text{sphalerite}) = 4 \text{ZnS} (\text{non-crystal}) + 4\Delta H / N_A, \quad (22)$$

Comparing states (21) and (22), one can acknowledge that if the states

$$(\text{Zn}_4\text{S}_4)^0 \text{ and } \text{Zn}_4\text{S}_4 (\text{crystal})$$

are energetically identical, the predissociation of the crystal cell in Fig. 7b may be presented as a transition



between energetically identical states if $\varepsilon=4\Delta H_{\text{subl}}/N_A$. So, in the cell Zn_4S_4 of sphalerite there are $2Z=8$ tetrahedral voids, half of which is populated by 4 zinc atoms. Remaining 4 voids can provide their space to Zn atoms at the moment of pre-dissociation of no more than 4 chemical bonds Zn-S in spectral experiment.

3. Following this example, we consider the cell of wurtzite, Zn_2S_2 , while $Z=2$. The cell can increase its potential energy through the resonance absorption of a photon with energy ε . Then, according to Fig. 7b we can write

$$(\text{Zn}_2\text{S}_2)^0 = (\text{Zn}_2\text{S}_2)^* + \varepsilon,$$

where $(\text{Zn}_2\text{S}_2)^0$ is the basic state of the cell and $(\text{Zn}_2\text{S}_2)^*$ is an excited state.

Sulfur anions form cubic close packing with tetrahedral voids [65]. Half of them are filled in with zinc cations, while the second half is empty. When four tetrahedral voids are temporarily filled in due to photon excitement, the part of the solid (4ZnS) will lose the particles' placement symmetry, and we will write



between energetically identical states if $\varepsilon=2\Delta H_{\text{subl}}/N_A$. Thus, in Zn_2S_2 of wurtzite there $2Z=4$ tetrahedral voids half of which is populated by 2 atoms of zinc. Remaining 2 nanovoids can provide their space to Zn atoms at the moment of pre-dissociation of no more than 2 chemical bonds Zn-S in spectral experiment.

These examples of crystal-chemical description of spectral experiment allow explaining that the atom transition from one tetrahedral void to another is the principal essence of crystal pre-dissociation under photons' action. Suppose that among absorbed photons there are photons which are satisfying the condition $\varepsilon = \varepsilon_{pr}$. Then the original function $\varepsilon = f(D_{subl}, Z, \varepsilon_{pr})$ may be presented as follows:

$$1/\lambda = \text{const} Z \Delta H_{subl}$$

that relates the wavelength λ of the ultraviolet radiation absorbed by the crystal to its sublimation and dissociation enthalpies ΔH [10, 43].

6. Crystal-chemical symbolism and system theory

In the general theory of systems, the category of "emergence" is used as an effective tool for studying natural, economic, and social objects. The system has emergent properties, i.e. properties that are not inherent in its subsystems and modules as well as the ensemble of its elements without system-forming bounds. System properties are not reduced to the sum of the properties of its components. In solid-state physics, the emergence can be expressed as follows: one particle is not a body. For example, the symmetry of the body is not applicable to the individual particle. The photon is a particle that is not subjected to disassembling in elements or subsystems. The system consisting of photons has emergent properties. For example, the photon gas, unlike the unique photon, is characterized by its temperature and entropy. In the solar cell, the photon is one of the components of the system "crystal – radiation". In this chapter, we consider one of the changes in the system emergence as an antenna process. In crystallography and crystal chemistry, the emergence is the appearance of new functional unities of crystal that are not reduced to a simple rearrangement of particles.

In the system classification, the emergence can be the basis of their systematics, representing the criterion feature of the system. Let us consider the single crystal as a set of interrelated atomic particles located in the respective specific order, i.e. as a system, and denote it with **S**. It has emergent properties. For example, a crystal system is characterized by the symmetry of the external shape as well as by the symmetry of the spatial location of atomic particles.

Authors of [9] define the crystal system **S** as a set of individuals belonging to a mineral species that are, in turn, present in the crystalline formations of the atoms of corresponding chemical elements; these sets of atoms can independently exist with further growth.

In crystalline systems, the crystallinity and size limit can serve as the unifying community feature. Work [9] describes the elements of such systems. Their reality makes it possible, for example, to measure the amount of substance in the initial stage of crystallization by the mole of seeds, the number of cosmic dust particles by the mole of dust, the amount of substance in real crystal by the mole of blocks that are broken by line and screw dislocations, nuclear, and other macroscopic defects. The substance of colloidal solutions may be measured by the mole of colloidal particles that they contain. Let us denote such elements with the letter **b**.

In this chapter we will consider the element **b** as a crystal system **S*** and characterize it by the element that corresponds to the symmetry of the crystal. Note that this element is denoted as **a**. In the first approximation, the element **a** is formed in an ideal crystal environment and is defined as a set of atoms of chemical elements; the number of these elements is limited and is equal to the multiplicity of regular point systems. The element **a**, that keeps the chemical composition of the crystal does not exist independently.

In connection with the definition of the element **a**, the special procedure for defining the substance quantity of a crystal consists of disassembling systems **S** and **S*** into new subsystems, i.e. into such systems where the internal laws correspond to the geometric theory of the structure of crystals. Such subsystems are identified by us with the element **a** and are identified as the structural elements of matter (elementary entity).

The practical value of disassembling such crystal systems is that for the first time we have an opportunity to relate the quantitatively geometrical properties of the crystal with the density of the matter and the mass of the atoms, and to describe other characteristics through these features.

This relation is based on the individuality of the ratio value of the regular points systems of crystalline space. That is why the ratio of the amount of element **a** present in relation to the crystal volume is its characteristic value. This value will be called the "density of substance quantity" with the measurement unit of a mole. It characterizes the number of structural elements of substance in the crystal volume. It is necessary to clarify that the other physical quantity, "density," is characterized not by quantity, but by weight. Therefore, it is obvious that the values of the "density of matter" and the "density of the amount of a substance" differ in terms of their physical nature.

The density of the amount of a substance was introduced into scientific practice only recently in [42] as a derived quantity stated in SI and marked with the letter σ . The unit σ represents the "moles per cubic meter." The crystal as a system is characterized by the ratio of the volume, v , of the amount of a substance to its volume, V . Therefore, the equations defining and linking it with other physical values are the following:

$$\sigma = v / V = \rho / M, \quad (23)$$

where M is the mass of a mole of a structural element of the substance or a structural element **a** of the subsystem **S*** in the system **S**; ρ is the density of matter.

The values σ for gases do not depend on the chemical nature. For example, according to Avogadro's law, σ is a gas under normal conditions equal 44.6 moles of molecules per cubic meter. The values σ for crystals are individualized and are determined by the formula derived from Eq. (23)

$$\sigma = \rho / \sum_{i=1}^n (k_i M_i), \quad (24)$$

where k_i is the multiplicity of a regular points system for atoms of i -sort; M_i is the mass of moles for atoms of i -sort. For example, the denominator of the ratio (24) for CaF_2 equals

$$4M_{\text{Ca}} + 8M_{\text{F}},$$

because the multiplicity of the regular points system for calcium atoms equals 4 and for fluorine atoms it equals 8. Taking into account the density of matter, the σ value for CaF_2 equals 10.2 kmol of element **a** in a cubic meter, and the mole of element **a** corresponds to the mole of elementary Bravais cells in the crystal.

In this chapter, we calculated σ values for simple substances and chemical compounds that are crystallizing in differently spaced symmetry groups. The multiplicity of regular points systems may differ from each other under calculation, so that the amount of element **a** in a given crystal system may vary by the number of included atoms. In this case, a unit mass of a substance will contain a different number of elements **a**. In other words, we can say that the phenomenon of polymorphism is a reflection of the state of a unit mass of a crystal with a different number of substances. For example, the multiplicity of a regular points system of carbon-12 in a diamond equals 8 and in graphite it equals 2. Thus, 0.012 kg of carbon-12 corresponds to either an 1/8 mole of diamond or a 1/4 mole of graphite. Let us explain the value of a mole of graphite. There are two sorts of carbon atoms with the same multiplicity of regular points systems in graphite. Thus, the denominator of relation (24) equals

$$2M_{\text{C1}} + M_{\text{C2}} = 4M_{\text{graphite}}$$

because $M_{\text{C1}} = M_{\text{C2}}$. The values σ are equal to 36.6 and 47.0 moles of elements **a** in a cubic meter of diamond and graphite, respectively.

The use of a multiplicity of a regular points system in calculations of substance amounts in crystals allows us to reveal completely unexpected correlations in numerous known experimental data. For example, the enthalpy values of gas-crystal phase transitions related to the mole of elements **a** correlate to the wavelengths of the absorption of substances in the ultraviolet region of the electromagnetic spectrum. The description of this correlation is presented in the next section, in which the element **a** of the crystal system is presented through the Bravais cell.

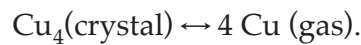
6.1. The photon and the crystal cell as elementary entities of matter

The mole is a unit of measure of an amount of substance, i.e. the number of atoms, molecules, ions, or other elementary entities of a substance (EES). We are adopting a definition of the mole that was presented at the 14th General Conference on Measures and Weights in 1971: "mole is equal to the amount of substance of a system containing in carbon-12 with a mass of 0.012 kg. In application of the mole, the elementary entities must be specified: they may be atoms, molecules, ions, electrons, or other particles or specified groups of particles" [12, 67], IUPAC, 1988).

The mole is applied to a gas without any difficulty. In a liquid, the specification of elementary entities often creates difficulties. In the application of the mole to a crystal, we propose specifying the elementary entities in accordance with the basic indicator of a crystal—its three-dimensional periodic structure.

The elementary cell will correspond to such an elementary entity. In this case, the elementary entity will be characterized by the number of formula units Z . For example, the formula of the elementary entity of fluorite is written as Ca_4F_8 ; Z will be equal to 4. Here it has been shown that the elementary entity corresponding to an elementary cell of the crystal is an object that is capable of absorbing a quantum of energy.

Let us examine this in the example of copper, for which the formula of the elementary entity is written as Cu_4 . Through the symbol ΔE we will denote the change in the energy of the crystal upon the dissociation of a mole of Cu_4 into an ideal atomic gas. The value of ΔE can be calculated based on Hess' law:



Under isobaric conditions, the heat of this reaction is equal to the enthalpy change ΔH . Then ΔE will be equal to the product of Z and the ΔH of the sublimation of copper:

$$\Delta E = Z \Delta H_{\text{subl}}$$

For copper at 1 atm and 25° C, according to [70], $\Delta E = 4 \cdot 80.7 = 323$ kcal/mol.

Let us assume that one of the mechanisms of radiation absorption by a crystal is resonance absorption by an elementary entity of a quantum of energy, $\epsilon = \Delta E / N_A$, where N_A is the Avogadro number. After resonance absorption, the transition of the elementary entity from a stable electronic state to an unstable state is possible without any change in energy. Such a transition is called "predissociation." It may also end in the dissociation of an elementary entity.

If the probability of absorption of an energy quantum ϵ makes it possible for the intensity of absorption to exceed the background level, an individual peak in the absorption spectrum of the crystal, or possibly a shelf, wing, or shoulder on a peak of a different nature can occur. Their positions on the absorption curve can be calculated from the generally known relationship between the wavelength and the energy of the quantum. In the present case, it is written as

$$\lambda = chN_A / \Delta E, \quad (25)$$

where h is the Planck constant and c is the speed of light. For copper, the value of λ is 887 Å. In the absorption spectrum of copper [56], this wavelength corresponds to a shelf in the 885–950 Å interval (Fig. 8).

From this standpoint, let us examine graphite, for which there are two modifications with the number of formula units Z : 4 and 6. Calculations of λ are 418 Å for $Z=4$ and 219 Å for $Z=6$. Since natural graphite is a concretion of these two modifications, the absorption curve of graphite should have two maximums corresponding to the values of ΔE for these two kinds of elementary entities. In fact, in spectrum [28] there are two such peaks that are not observed on amorphous samples of carbon (see Fig. 8).

Eq. (24) and (25) offer a means for predicting the positions of the absorption peak maximum for another modification of carbon, namely diamond, the structure of which, according to [27, 70], is characterized by a single $Z=8$ and ΔH_{atom} of atomization 1364 kcal/mol. The maximum of the sought peak should lie in the 210 Å region. This absorption band of diamond has not been investigated [56], but it can be obtained in principle. Germanium and silicon have a structure analogous to that of diamond. The values of λ calculated for these elementary entities, 395 and 331 Å, respectively, practically coincide with the maximum at 395 Å on the germanium absorption curve and the wing at 330 Å for the silicon [56].

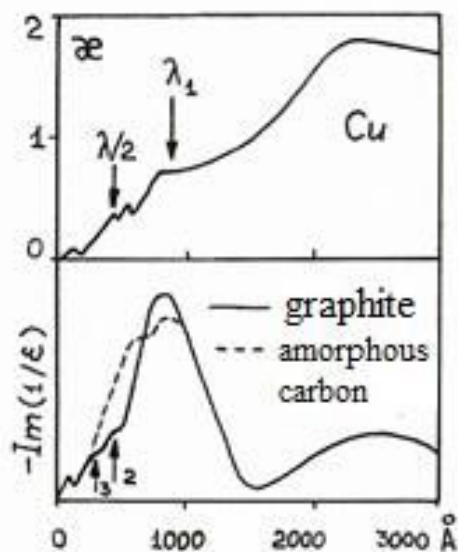


Figure 8. Absorption spectra (the absorptivity to the wavelength) of copper, graphite, and amorphous carbon [28, 56].

7. Metallic nano-cluster open new ways to enhancement of solar cell' efficiency

Novel high effective solar devices are based not only on semiconductors (bulk or thin films), but also on nano-scaled clustered structures. These structures are fabricated using various chemical technologies.

For example, Chen et al. describe synthesis of silver particles on copper substrates using ethanol-based solution (Chen et al., 2014). Previously we have reported success of wet chemical

technology in manufacture of Ag/Co-nanocluster wires forming the contact grid for common silicon-based solar cells with enhanced efficiency [54].

Along with structural and morphological analysis the interpretation of experimental electrical measurements is also of great importance. Basing on our analysis of manufactured solar devices we should note that semi-classical theories widely used for interpreting properties of semiconductor-based devices are not always applicable for end-description of characteristics observed experimentally. In particular, role of semiconductor channel carrier concentration is analysed by [72]. Carrier escape mechanisms can also play a significant role in effective function of solar devices [66].

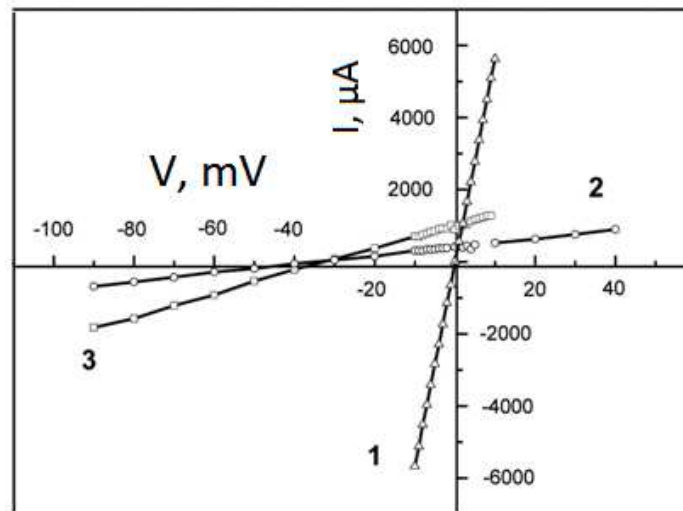


Figure 9. Current–voltage dependences for (1) a contact SGE (Stripe-Geometry Element) made of silver, (2) a contact SGE with copper clusters positioned in the silver pores, and (3) SGE with a copper layer positioned on the surface and with copper clusters positioned in the silver pores.

Current-voltage characteristics are of special importance and interest. Their analysis is helpful for estimation of efficiency limitations in solar cells [29]. Open-circuit voltage and the driving force of charge separation in solar cells based on different junctions are particular features defining efficiency of the device (Hara et al., 2013).

Below we report our experimental results and first attempts to model them.

The experimental setup was described in detail previously [54]. The measurements were performed for two specimens placed in a box with black walls and a solar simulator. The main part of the experimental equipment was a tungsten contact-needle. Its role is explained below. The experimental results are presented in Figs. 9-10.

As we can see, the curve 1 is the current–voltage dependence for the initial silver contact SGEs (Stripe-Geometry Element) arranged at a wafer surface. Other curves in Fig. 9 are the current–voltage dependences for contacts obtained after copper deposition. All the curves support the metallic conduction of the contact SGEs. The distinction between them resides in the fact that, in the case of contacts with copper clusters, these curves do not pass through the origin for

either the forward current or for the back one. The phenomenon of a current flowing through a metal in the absence of an applied electric field is not outlined in the literature. In our experiment, the luminous current of 450 μA flows along the contact with copper clusters disposed only in silver pores and that of 900 μA flows along the contact with copper clusters disposed in the pores and at the silver surface.

Of fundamental importance is the fact that, in the absence of an applied electric field, the electric current continues to flow along the same samples when a solar simulator was taken out of service. The luminous and dark currents flowing along the contact SGEs are presented in Fig. 10. As can be seen, under the zero bias, in the case of darkness, the generation of charge carriers is kept constant in the duration of the experiment. In the silver contact, the dark current is associated with charge carriers generated in the contact itself. The silver clusters positioned in pores and at the silver surface serve as a source of charge carriers for the dark current.

We should note that various nanoscaled solar devices are proposed for high-effective photon harvesting [40, 74, 76, 77]. Now let us describe our results and first attempts of their numerical simulation.

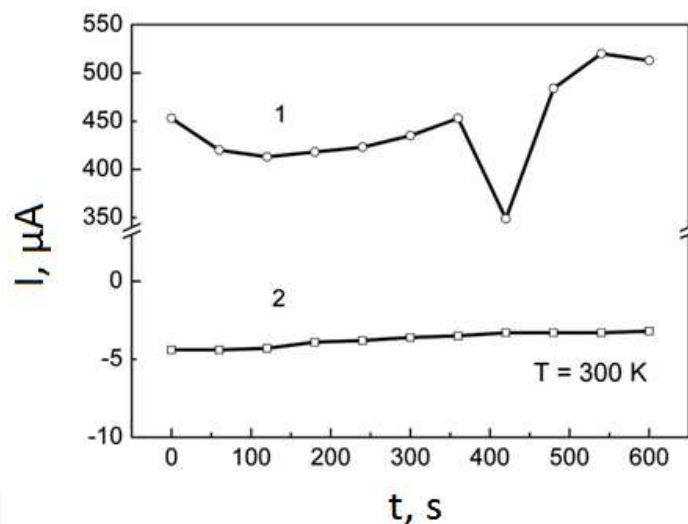


Figure 10. Time dependencies of dark and luminous currents in the absence of applied bias at contact SGEs (Stripe-Geometry Element) with copper clusters positioned in silver pores.

As we have shown previously [53], the first attempting for explanation is to consider a Si-based p-n-junction with Ag/Cu-contacts with different heights of barriers formed at the metal-semiconductor interfaces: $\phi_{\text{Beff}} = \phi_{\text{Bn}} + \phi_{\text{Bp}} \sim 0.05 \text{ eV}$ (this value characterizes the effective barrier heights for electrons and holes, respectively) [53] and Refs. therein) and, on the other side, the barrier may be formed due to the difference of work functions of the contact metals: $\phi_{\text{B}} = \phi_{\text{Cu}} - \phi_{\text{Ag}} = 0.17 \text{ eV}$ [53] and Refs. therein). Remembering how the solar cell operates (under illumination the device harvests generated carriers and in darkness our active element produces practically no work, therefore, it should be no current!), we tried to calculate possible currents according to the semi-classical theory of semiconductor devices [53] and Refs. therein):

$$I_{Cu} = A_{el} A^{**} T^2 T_{tun} \exp(-e\phi_{B_{eff}} / k_B T) \exp(eV_a / k_B T), \quad (26)$$

where I_{Cu} denotes the current producing by illumination of the sample where Cu-atoms are in Ag-pores and on the surface of the Ag-finger, A_{el} is an electrical area of the contact, A^{**} is the effective Richardson constant, T_{tun} is a coefficient of the barrier tunneling transparency, k_B is the Boltzmann constant, V_a is an applied voltage.

What can we obtain for a dark current, when only the deformation of clusters in the contact stripe due to difference between the lattice constants of silver and copper can change the work function and the barrier height, respectively?

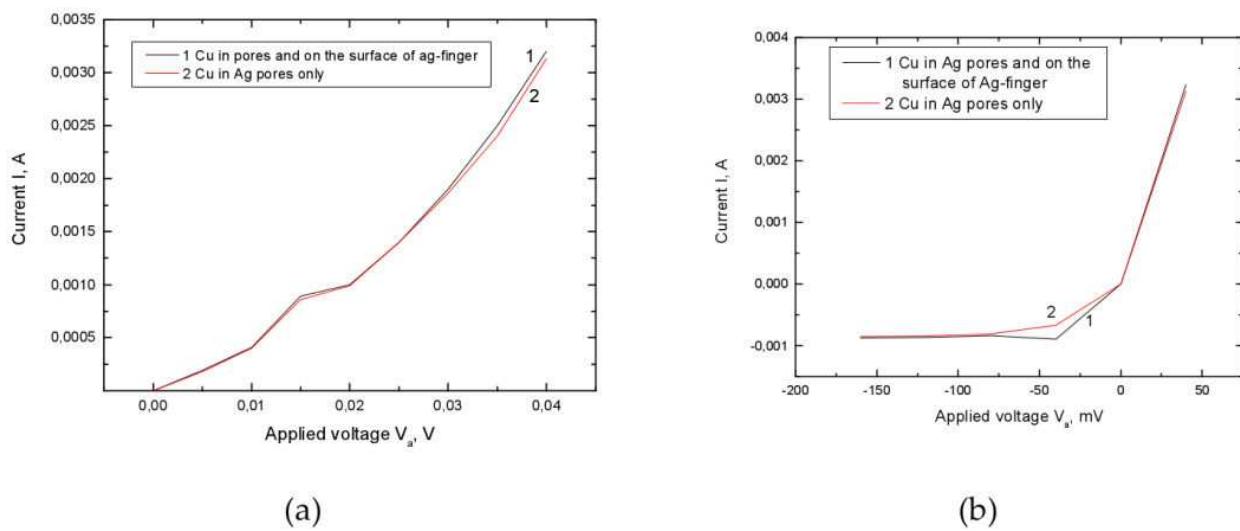


Figure 11. (a)-current-voltage characteristics (numerical experiment!) of the Cu/Ag-cluster contacts of the Si-based solar cell: the calculation is performed according to the expressions (65)-(66): (a)-“forward” sections of the experimental dependencies, (b)-both sections of the experimental dependencies.

The expression is as follows:

$$I_{Cu1} = A_{el} A^{**} T^2 T_{tun} \exp(-e\phi_{B_{1f}} / k_B T) \exp(eV_a / k_B T), \quad (27)$$

where I_{Cu1} denotes the current observed under illumination of the sample with cu-atom in Ag-pores of the Ag-finger only; we should note that values of the tunneling transparency coefficient are in the range $10^{-7} - 10^{-5}$ (they are determined numerically basing on the experimental data). Fig. 11 show results of the numerical experiment.

As one can see, the numerical experiment performed in the region of very small applied bias (up to 40 mV) produces only a qualitative agreement with the measurements. First, there is no a “solar-cell feature” (calculated IVCs are beginning from zero unlike that of the illuminated solar cells), second, the values of experimental and calculated currents are also different. The semi-classical approximation (we introduced it by using the tunneling transparency coeffi-

cient) does not take into account all features of the conductivity of nanoscaled cluster structures. Before we discuss the further results we would like to say some words about current-voltage dependencies of nanostructures. The overlap energy between different sites is related to the width of the energy bands. The second factor is disorder-induced broadening of the energy levels. If the ratio of these values is small, it is hard to match the width of the energy level on one site with that of a neighboring site to that the allowed energies do not overlap and there is no appreciable conductivity through the sample. On the other hand, if the ratio is large, the energy levels easily overlap and we have bands of allowed energy, so that there are extended wave functions and a large conductance through the sample [53] and Refs. therein).

The current flowing along a silver contact with copper clusters is induced by charge carriers generated in the semiconductor section of the wafer when the solar cell is illuminated. The density of carriers generated within the p - n junction is two orders of magnitude higher than that which occurred in the copper clusters, because the luminous current is two orders of magnitude larger than the dark one (Fig. 10).

Depositing copper onto silver does not result in the formation of the silver-copper solid solution. The contact between the crystal structures assures the electrical potential difference. The difference is inadequate to generate the charge carriers. However, the contact between the silver-copper crystal structures may result in the compressive deformation of a metallic SGE and in a decrease in the electron work function for copper clusters.

It is our opinion that, in darkness, charge carriers generated by copper clusters within a contact SGE (Stripe-Geometry Element), which is the component part of the solar cell, are governed by the deformation of the SGE [25]. It is known [63] that the deformation of metal cluster structures may also result in high temperature superconductivity. On the other hand, the experimental measurements are made with special needles which are mechanically contacting with the investigated structure. We have to account additional "external" mechanical deformation which, in turn, may cause appearance of additional external electric field without any voltage source. Going back to Chapter 5 of our book [54], see the scenarios about positive and negative pressures!) we should note that this "needle"-caused deformation brings the system "metallic Cu/Ag-cluster contact-Si-semiconductor surface" to the state with different local pressures, for example, negative pressure under the needle on the front side of the structure ($-F_{1el}$) and positive pressure under clusters on the semiconductor surface ($+F_{2el}$). Thus, we have no zero resultant force ($F_{1el}-F_{2el}$) acting between the electrons localized in the clusters. We suppose that these local pressures are of different values, and the resultant stress is $\sigma=(F_1-F_2)/A_{cluster}$, where $A_{cluster}$ is a cross-sectional area of the Cu/Ag-cluster. The second possibility to observe the dark current is the effect of nanovoids introduced as the first level of the structural organization of the crystal (see text above) serving as drains and sources for charge carriers. More detailed: the nanovoids play one of principal roles in the processes of pre-dissociation of atoms building basic semiconductors for photovoltaics: Si, ZnSe, ZnTe, and other wide-gap materials. Experimental current-voltage characteristics of the structures can only be approximately described by different theoretical models, while the charge carriers moving from the left contact to the right one (direct current) and in opposite direction (reverse current) are experiencing not only the barrier effects but they dissipate and exchange their energy in and with nanovoids.

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