

**MATHEMATICAL MODELING OF THE MIXING ZONE
FOR GETTING BIMETALLIC COMPOUND**

Stanislav L. Kim

Institute of Applied Mechanics, Ural Branch RAS, 426-67, Izhevsk, ul.T.Baramzinoy, 34

Abstract

A mathematical model of the formation of atomic bonds in metals and alloys, based on the electrostatic interaction between the outer electron shells of atoms of chemical elements.

Key words: *mathematical model, the interatomic bonds, the electron shell of atoms, the potential, the electron density, bimetallic compound.*

INTRODUCTION

According to modern notions [1], the interaction of atoms with each other is carried out mainly by the Coulomb interaction of their outer electron shells, formed by the valence electrons. Because the metal materials and completing electronic density of the outer electron shells is much smaller than the density and occupancy of the inner shells, we can assume that the influence of quantum effects in the interatomic interaction between two atoms is negligible. If we assume that the electronic configurations of atoms are already known, then the potential energy of their interaction (interatomic potential) can be found as the Coulomb interaction energy. Assuming the distribution function of the electron density in the atom-known, we can define the parameters of this distribution from the experimental characteristics of single-component metallic crystals. These options can be found by solving the inverse problem of electrostatics, and must appear in the expression for the interatomic potential. This circumstance is of fundamental importance because if we find the electron density distribution in the atom, it becomes possible in principle to solve the problem of describing multicomponent compounds and in particular - bimetal. Simulating the appearance of electron density distribution in the atom, you can pick it up so that the calculated values of the known characteristics of the crystals would have been close to the experimental values. Then we can assume that the form of electronic distribution most closely resembles the one that takes place in real atoms.

MATHEMATICAL MODEL OF INTERACTION OF ATOMS

Potential of the electrostatic interaction between atoms is entirely dependent on the nature of the electron density distribution in atoms. In this model, the electron density is defined as the density of only the outer valence electron shells of atoms. This is because it is the socialization of the valence electrons of the atoms leads to the formation of atomic bonds in solids [2].

Assume that the charge of the outer shells of the atom q_1 evenly distributed on the surface of a thin sphere of radius R_1 , centered on the nucleus, and offset part of the nuclear charge.

Consider the interaction of atoms 1 and 2 with the parameters of distributions (R_1, q_1) and (R_2, q_2) respectively. Let R be the distance between the centers of atoms (Fig. 1). As justified above, the interaction between atoms is due only to electrostatic forces. Then the potential of interatomic interaction can be represented as:

$$\varphi(R) = \varphi_{c_1-c_2}(R) + \varphi_{c_1-n_2}(R) + \varphi_{n_1-c_2}(R) + \varphi_{n_1-n_2}(R), \quad (1)$$

where the first term corresponds to the interaction of the outer electron shells of atoms 1 and 2 with each other, the second and third - shell nuclei, and the last - the interaction of the nuclei.

Each term of equation (1) is obtained by integrating the volume density of the Coulomb interaction energy of the electron distribution.

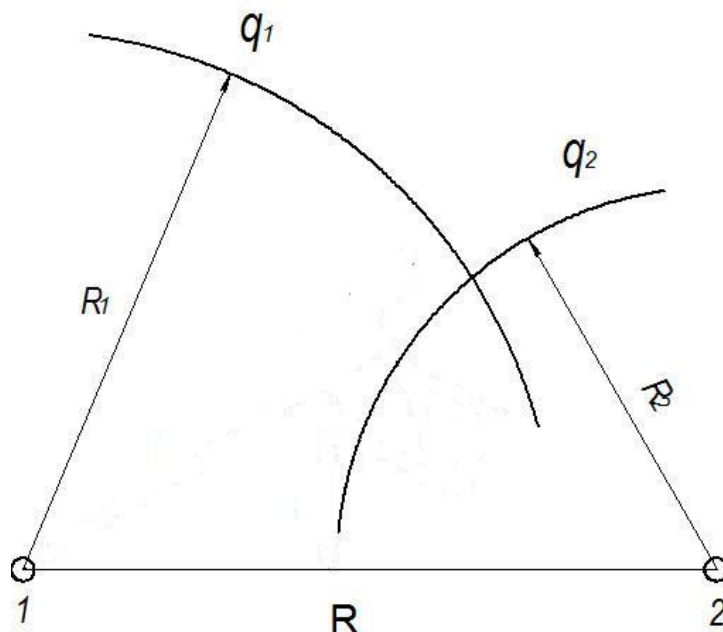


Fig. 1. Scheme of the overlap of electron shells of atoms 1 and 2

The interaction energy of nuclei with each other is determined by:

$$\varphi_{n_1-n_2}(R) = k \frac{q_1 q_2}{R}, \quad (2)$$

where - the size factor: $k = 14,4 \text{ (eV} \cdot \text{\AA} / e^2)$.

We denote the potential created by the outer electronic shells of atom 1 at a distance from the nucleus, and through - the corresponding potential created by the electron shells of the second atom. Then (Fig. 1):

$$\Phi_1(r) = \begin{cases} k \frac{q_1}{R_1}, & \text{for } r < R_1 \\ k \frac{q_1}{r}, & \text{for } r \geq R_1 \end{cases} \quad (3)$$

$$\Phi_2(r) = \begin{cases} k \frac{q_2}{R_2}, & \text{for } r < R_2 \\ k \frac{q_2}{r}, & \text{for } r \geq R_2 \end{cases} \quad (4)$$

Interaction energy of charged spheres with nuclei of neighboring atoms can be written as a system of equations:

$$\varphi_{c_1} - \varphi_{c_2} = \Phi_1(R) \cdot q_2 = \begin{cases} -k \frac{q_1 q_2}{R_1}, & \text{for } R < R_1 \\ -k \frac{q_1 q_2}{R}, & \text{for } R \geq R_1 \end{cases}; \quad (5)$$

$$\varphi_{c_2 - n_1} = \Phi_2(R) \cdot q_1 = \begin{cases} -k \frac{q_1 q_2}{R_2}, & \text{for } R < R_2 \\ -k \frac{q_1 q_2}{R}, & \text{for } R \geq R_2 \end{cases}. \quad (6)$$

Consider the interaction of shells 1 and 2 with each other. It is obvious that at large interatomic distances, when the electron shells do not overlap, their interaction with each other is equal. Then:

$$\varphi_{c_1 - c_2} = k \frac{q_1 q_2}{R}, \quad (7)$$

which coincides with the interaction energy of nuclei from the equation (2).

Consider the case of overlapping electron shells. The condition of the overlap can be written in the form of inequality $R < R_1 + R_2$.

Let $\vec{r}_1$ - the radius vector drawn from the center of the nucleus of the atom 1 in one of the points of the electron shell of atom 2, near which is the charge dq_2 , that is, one of the points of the sphere of atom 2. Then:

$$\varphi_{c_1 - c_2} = \int_{\text{no sphere 2}} \Phi_1(r) dq_2. \quad (8)$$

Under the charge dq_2 in equation (8) should be understood, some charge a shell of the second atom, located on a thin ring of radius h and width dl (Fig. 1). Distance from any point of the ring to the nuclei 1 and 2 remain unchanged. Then:

$$dq_2 = \frac{q_2}{4\pi R_2^2} 2\pi h dl = k \frac{q_2}{2RR_2} r_1 dr_1. \quad (9)$$

Interatomic Potential must be represented in the form of two integrals, the first of which integration is performed over the region scope of atom 2, located inside a sphere with a radius R_1 , and the second - for the remainder of the scope of atom 2:

$$\varphi_{c_1} - \varphi_{c_2} = k \frac{q_1 q_2}{2RR_2} \int_{|R-R_2|}^{R_1} \frac{r_1}{R_1} dr_1 + \int_{R_1}^{R+R_2} k \frac{q_1 q_2}{2R_2 R} dr_1. \quad (10)$$

After performing the appropriate integration, we obtain:

$$\varphi_{c_1} - \varphi_{c_2} = k \frac{q_1 q_2}{2} \left[\frac{1}{R} + \frac{1}{R_1} + \frac{1}{R_2} - \frac{R^2 + R_1^2 + R_2^2}{2RR_1R_2} \right]. \quad (11)$$

Assume that $R_1 > R_2$. Then, for the interatomic potential (1) subject to equations (2-11) is written as a piecewise-smooth function:

$$\varphi(R) = \begin{cases} k \frac{q_1 q_2}{2} \left[\frac{3}{R} - \frac{1}{R_1} - \frac{1}{R_2} - \frac{R^2 + R_1^2 + R_2^2}{2RR_1R_2} \right], & \text{npu } R \leq R_2 \\ k \frac{q_1 q_2}{2} \left[\frac{1}{R} - \frac{1}{R_1} + \frac{1}{R_2} - \frac{R^2 + R_1^2 + R_2^2}{2RR_1R_2} \right], & \text{npu } R_2 < R \leq R_1 \\ k \frac{q_1 q_2}{2} \left[-\frac{1}{R} + \frac{1}{R_1} + \frac{1}{R_2} - \frac{R^2 + R_1^2 + R_2^2}{2RR_1R_2} \right], & \text{npu } R_1 < R \leq R_1 + R_2 \\ 0, & \text{npu } R > R_1 + R_2 \end{cases}. \quad (12)$$

If the interacting atoms are identical, ie and, the expression for the interatomic potential can be simplified:

$$\varphi(R) = \begin{cases} kq_1^2 \left[\frac{1}{R} - \frac{1}{R_1} - \frac{R}{4R_1^2} \right], & \text{npu } 0 < R \leq R_1 \\ kq_1^2 \left[\frac{1}{R_1} - \frac{1}{R} - \frac{R}{4R_1^2} \right], & \text{npu } R_1 < R \leq 2R_1 \\ 0, & \text{npu } R \geq 2R_1 \end{cases} \quad (13)$$

Fig. 2 is a kind of interatomic potential on the equation (12) and its component parts. As can be seen from the graph, the minimum of interatomic potential is in R_2 distance.

Internal energy of a single-component crystal can be represented as the sum of the energies of pair interatomic interactions:

$$U(a) = \frac{1}{2} \sum_j \varphi(r_j), \quad (14)$$

were $\varphi(r_j)$ has the form of equation (13), a - lattice parameter.

Conditions for the stability of the crystal lattice with the experimental values of the lattice parameter a_0 and the sublimation energy E_S can be written as:

$$U(a_0) = -E_s, \quad \frac{dU}{da_0} = 0, \quad \sum_j r_j \frac{d\varphi}{dr_j} = 0. \quad (15)$$

For definiteness, let $R_1/a_0 = 1$. Then, for the chemical elements with face-centered cubic (FCC) calculated from the dependence (14) energy-component crystal $U(a)$ will have the form shown in Fig.

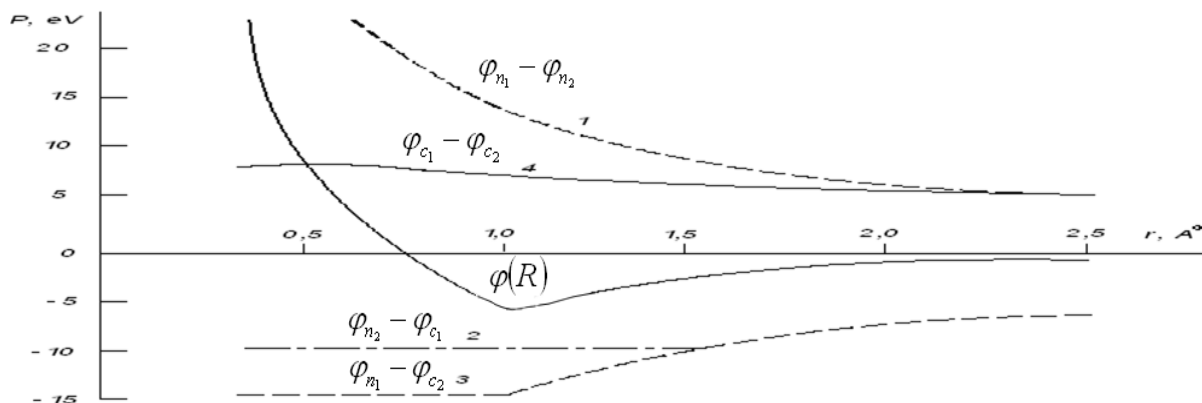


Fig. 2. Form of the interatomic potential by equation (12) (solid line) and its component parts:

$$\varphi_{n_1} - \varphi_{n_2}, \varphi_{n_2} - \varphi_{c_1}, \varphi_{n_1} - \varphi_{c_2}, \varphi_{c_1} - \varphi_{c_2} \text{ when } q_1=1, R_1=1.5\text{\AA} \text{ and } q_2=1, R_2=1.0\text{\AA}$$

3.

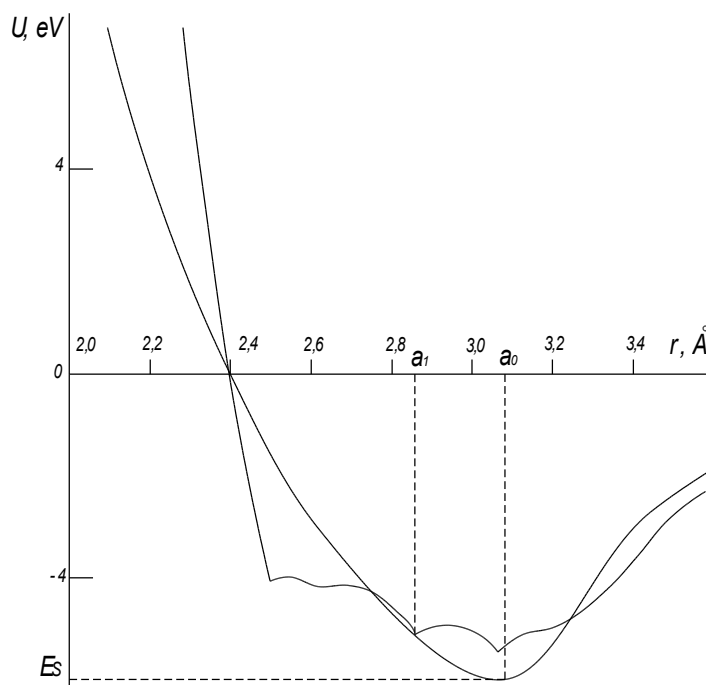


Fig. 3. Dependence of the internal energy of the crystal of a chemical element with the FCC the size of the unit cell a and a scheme for determining the equilibrium value lattice parameter

As can be seen from the graph (Fig. 3), the dependence of the internal energy of the lattice parameter is also a piecewise smooth function. Availability intervals piecewise smoothness is due to the influence of interaction not only atoms 1 and 2 with each other, but also with other atoms, forming a crystal lattice, the electronic sphere which fall within the scope of the potential interaction between atoms 1 and 2 ($R < R_1 + R_2$).

Formally, the condition (15) can be performed at multiple points (eg, break points of the curve). However, the values of the lattice parameter at these points are not physically acceptable. A similar dependence $U(a)$ is obtained for a different choice R_l .

In view of the mentioned circumstances, it becomes obvious that the derivative dU/da must be found numerically, using finite-difference methods. At the same time step Δa of numerical differentiation should be chosen large enough to encompass several piecewise-smooth intervals (Fig. 3).

MATHEMATICAL MODELING

Take a test lattice parameter a_1 near the expected value for a sufficiently long interval Δa . The values of internal energy in the points $a_1 - \Delta a$, a_1 , $a_1 + \Delta a$ denoted, respectively, U_1 , U_2 , U_3 ; ie., $U_1 = U(a_1 - \Delta a)$, $U_2 = U(a_1)$, $U_3 = U(a_1 + \Delta a)$. Through the points obtained will hold a parabola. Position of the minimum of this parabola must specify the equilibrium a_0 lattice parameter. Then the value of the minimum energy parabola should correspond to the value of the sublimation energy E_s . By varying the value of R_l can consistently pick her up so that the lattice parameter found from the above scheme, consistent with the experimental value a_0 . In this case, the charge of the shell is selected from the condition (15), taking into account the depth of the minimum of the parabola.

Equation (15) that the values of R_l are determined only by the type of crystal lattice with a value a_0 . Therefore, for items with the same type of crystal lattice ratio R_l/a_0 should remain unchanged. Indeed, calculations show that for FCC metals $R_l/a_0 = 0,75007$. This means that the interatomic interaction is nonzero only for atoms at a distance of the first coordination spheres. Atoms being located at a distance of the first coordination sphere ($r_1=0,707$; $a_0 < R_l$) repel each other. A atoms in the nodes of the second - fourth spheres, have a mutual attraction

A somewhat different picture is obtained for crystals with a body-centered (BCC) lattice, where $R_l/a_0 = 1,00249$. Potential in the BCC lattice is shestisfermym. The first two areas are working on the repulsion, while the third - the sixth - the attraction.

RESULTS AND DISCUSSION

Absolute value R_l and the charge found on the above scheme for most elements with the FCC and BCC, along with the original experimental values of the lattice parameter and the energy of sublimation are given in Table 1.

It should be noted that the values of R_l and the outer shells of charge q_l , given in (Table 1) are not the only solutions obtained by the above algorithm. For example, an alternative to Fe can be $R_l/a_0=2,07$ and $q_l=0,762$. However, with this decision in equation (14) must interact atoms at a distance up to the 12th coordination sphere, which seems unlikely from a physical point of view.

The internal energy of the ordered alloy per structural unit was found from the relation:

$$U_{cni}(a) = \frac{1}{2} \sum_m \sum_n \Phi_{mn}(r_{mn}), \quad (16)$$

where the index m indicates the number and type of atoms in this structural unit, for example, $Fe1$, $Fe2$, $Fe3$, $Al1$ $Al1$ in the structural unit Fe_3Al of the alloy with a superstructure DO_3 ; n - the number and type of atoms from the environment of the first in the limits of the number of coordination spheres; r_{mn} - the interatomic distance is proportional lattice parameter of the alloy a .

The equilibrium lattice parameter a_0 determined by minimizing the function U_{cni} approximating parabola.

As the internal energy of the alloy was taken at the energy of pair interaction of its atoms, determined by the method of [10], taking into account the heat of mixing [11]. Comparison of the values found for the binding energy of binary alloys was carried out with the energy value of the sublimation E_s .

According to the above algorithm, we calculated the lattice parameters and binding energies in these alloys arranged in a superstructure of type B2, DO_3 , $L1_2$, in comparison with known experimental data (Table 2).

Due to the parabolic approximation of the internal energy for the calculated values a_0 , U_{cni} (Table 2) has a slight discrepancy.

Table 1. Experimental data and calculated values R_1 and q_1
for a number of chemical elements

Chemical element	Experimental data [1, 3, 4]			Calculated values	
	Lattice type	The lattice parameter a_0 , Å	Sublimation energy E_s , eV	The radius of interaction R_1 , Å	Charge of the outer shell q_1/e
Li	BCC	3,509	1,650	3,5177	0,5014
Na		4,291	1,130	4,3017	0,4589
K		5,247	0,941	5,2601	0,4630
Rb		5,700	0,858	5,7142	0,4608
Cs		6,140	0,827	6,1523	0,4696
V		3,028	5,300	3,0355	0,8348
Cr		2,885	4,100	2,8922	0,7167
Fe		2,866	4,290	2,8731	0,7307
Nb		3,301	7,470	3,3092	1,5566
Mo		3,147	6,810	3,1548	0,9647
Ba		5,025	1,860	5,0375	0,6371
W		3,165	8,660	3,1729	1,0909
Eu		4,606	1,800	4,6175	0,6000

Ta	FCC	3,805	8,089	3,8145	1,1561
Pa		3,925	5,460	3,9348	0,9647
Al		4,049	3,340	3,0370	0,6725
Ca		5,582	1,825	4,1869	0,5836
Ni		3,524	4,435	2,6432	0,7229
Cu		3,615	3,500	2,7115	0,6504
Rh		3,803	5,752	2,8525	0,8552
Pd		3,889	3,936	2,9170	0,7154
Ag		4,086	2,960	3,0648	0,6359
Ir		3,839	6,930	2,8795	0,9432
Pt		3,923	5,852	2,9425	0,8762
Au		4,079	3,780	3,0595	0,7180
Ce		5,161	4,770	3,8711	0,9073
Pr		5,160	3,900	3,8704	0,8203
Yb		5,486	1,600	4,1149	0,5418

Indeed, these numbers depend not only on the type of function $U(a)$, but also the choice of the initial value a_1 and step size Δa (Fig. 3).

In calculating the value a_1 was set by a number of angstroms, the closest to the experimental value. Trial step Δa is $0,2a_1$. Table 2 shows that in alloys with a superstructure such as $B2$ the calculated values of lattice parameters are less well-known experimental values. The exceptions are the alloys $AlFe$ and $AlPd$, в которых $a_{0_{расч}}$ in which almost coincides with the experimental value. For some alloys ($AgPr$, $AuCs$, $NaAl$) difference is quite significant (up to 20% in $AuCs$). This is explained by differences in the shells of the components (q_1 , R_1 and q_2 , R_2) and as a consequence, a large number of singularities on the chart $U_{cнл}(a)$. In alloys with superstructures $D0_3$ and $L1_2$ deviations $a_{0_{расч}}$ from $a_{0_{эксп}}$ can as a positive and the negative side.

Thus, in the framework of the developed mathematical model that adequately describes the interaction of atoms in metals and alloys, taking into account only the Coulomb forces of mutual attraction and the assumption that the density of the electron shells of valence electrons of the atoms represented by the function of "smearing" near the surface of thin spheres of radius R_1 , targeted and tested interatomic potential of metals and alloys.

Table 2. The calculated and experimental equilibrium characteristics of some binary alloys with superstructures type $B2$, $D0_3$, $L1_2$

Type of superstructure	Alloy	a_0 , Å calculation	a_0 , Å [1, 3-9]	$U_{\text{calc}}(a)$, ϑB calculation	E_s , ϑB [1, 3-9]
$B2$	<i>AgCe</i>	3,718	3,740	7,235	7,730
	<i>AgLi</i>	3,003	3,174	4,249	4,610
	<i>AgPr</i>	3,458	3,735-3,739	6,551	6,860
	<i>AlFe</i>	2,987	2,900	7,448	7,630
	<i>AlIr</i>	2,925	2,977	9,864	10,270
	<i>AlNi</i>	2,809	2,887	7,201	7,775
	<i>AlPd</i>	3,096	3,030	7,286	7,276
	<i>AlPr</i>	3,514	3,820	6,998	7,240
	<i>AlRh</i>	2,933	2,990	8,751	9,092
	<i>AuCs</i>	3,360	4,263	3,677	4,607
	<i>AuPr</i>	3,386	3,680	7,118	7,680
	<i>CuPd</i>	2,883	2,994	7,489	7,436
	<i>FeRh</i>	2,915	2,987	10,043	10,042
	<i>NaAl</i>	3,037	3,730	4,505	4,470
$D0_3$	<i>AlCu₃</i>	5,843	5,900	13,500	13,840
	<i>AlFe₃</i>	6,032	5,780	15,823	16,210
	<i>AlCe₃</i>	4,932	4,985-5,013	14,884	17,650
	<i>AlNi₃</i>	3,975	3,560	15,123	16,645
	<i>AlPr₃</i>	5,453	4,950-5,007	14,295	15,040
	<i>AlPt₃</i>	4,374	3,876	19,981	20,896
$L1_3$	<i>Cu₃Pd</i>	3,821	3,650	15,927	14,436
	<i>Cu₃Au</i>	3,797	3,750	15,283	14,280
	<i>Cu₃Pt</i>	3,809	3,68	17,566	16,352
	<i>FePd₃</i>	3,899	3,848-3,851	16,298	16,098
	<i>Ir₃Ta</i>	3,822	3,861-3,889	29,383	28,879
	<i>Ir₃V</i>	3,897	3,812	25,812	26,090
	<i>NbRh₃</i>	3,815	3,865	25,309	24,726
$L1_3$	<i>Pt₃Zn</i>	3,869	3,890	18,343	18,906

	Rh_3Sc	3,938	3,900	21,477	21,256
	Rh_3Ta	4,034	3,860	25,794	25,345
	Rh_3Th	3,829	4,139	24,094	23,182
	Rh_3V	3,897	3,795	23,016	22,556

CONCLUSION

Based on the electrostatic interaction between the outer electron shells of atoms of chemical elements developed a mathematical model that adequately describes the formation of atomic bonds in metals and alloys.

REFERENCES

1. Kittel. C. Introduction to Solid State Physics. Moscow: Nauka, 1978. 792 sec.
2. Solovyov, SD, Korablev GA Physico-chemical basis of education bimetallic compounds Vestnik IzhSTU. 2006. № 1. S. 34-39.
3. SS Gorelik, LN Rastorguev, Skakov YA X-ray diffraction and electron-optical analysis. Application. Moscow: Metallurgiya, 1970. 107.
4. Orlov AN, Trushin YV Energy of point defects. Moscow: Energoatomizdat, 1983. 82.
5. Bullock AE Structure and Properties of Binary Metallic Systems, Handbook in 4 Vols, Moscow: Fizmatgiz, 1962. 856 sec.
6. M. Hansen, K. Andreko Structural Properties of Binary Alloys / Handbook 2 Vols, Moscow: Metallurgiya, 1962. 563 sec.
7. Elliott, RP Constitution of Binary Alloys / Guide in 2 volumes. Ed. MI Novikov and IL Ryelberga Moscow: Metallurgiya, 1970. 652.
8. Baranov, MA, MD Starostenkov The calculation of equilibrium properties of metallic systems in the semiclassical approximation. Dep. VINITI, 1984. - № 3712-84. 31 with.
9. Baranov, MA, MD Starostenkov Kvazielektrostatichesky approach to the description of metallic systems, Preprint. Barnaul: Altai State Technical University, 1998. 40.
10. Solovyov, SD, Korablev GA Kodolov VI Calculation of activation energy of bulk diffusion and self-diffusion of elements in solids, "Khim and mesoscopic. Izhevsk: IPM RAS, 2005. V. 7, № 1. S. 31-40.
11. Urusov VS Theory of isomorphous miscibility. Moscow: Nauka, 1977. 265.