

# SPHERICAL SYMMETRY OF ELECTRONIC SHELLS OF ATOMS AND CRYSTAL STABILITY

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**Abstract.** The inner energy of a crystal is submitted only by pair atomic interactions. Distribution of electronic density of atom was supposed stationary, undeformable at interaction of atoms and it was represented as two spherical symmetrical shells - internal and external. The density of an internal shell was approximated by Gauss function and the density of external one – by function centered on a nucleus and reaching a maximum on some distance from a nucleus. Interactions between atoms in a crystal were represented by pair central potentials and were provided both electrostatic forces and forces of mutual repulsing of electronic shells. The density of energy of mutual repulsing of electronic shells of interacting atoms was accepted proportional to product of their electronic densities. The analytical shape of the appropriate interatomic potential was received and then was used as for definition of parameters of functions of electronic density distributions, and for the description of crystal properties. For the majority of alloys of simple and transitive metals with B2 superstructure there is a satisfactory conformity between the designed and experimentally measured values of lattice parameter. For the alloys formed by atoms of alkaline and alkaline-lands metals results of calculations are contrasted with experiment. Because the interatomic potential is not adhered to a concrete crystal lattice, within the framework of the offered approach there is possible the description of multicomponent substances.

## Introduction

Exaggeration will not tell, that all processes in environmental us world processes to a greater or lesser extent are determined by that how atoms interact between themselves and form those or other substances. Necessity of construction of the adequate quantitative description of interatomic interactions is obvious as from only scientific (a step for a way to understanding of the structure of substance) and with practical points of view. Especially actual such construction is represented in modern conditions at development of technologies of the future and perfection of methods of computer modeling of a condition of substance.

To present time it is possible to allocate two basic approaches to construction of such description – first principle and semi-empirical ones. First of them is based on definition of electronic wave functions in a crystal or a molecule proceeding from numbers of elements of the atoms forming this or that substance and the decision of Schrödinger equations for system of electrons and nucleus. Such approach is represented rather tempting. However the direct decision of a similar problem appears impossible even because of huge number of particles interacting among themselves. In this connection it is inevitable implementation a lot of simplifying assumptions, corrections and boundary conditions. Those, for example, are one-electronic approach, approach of located atomic orbital, restriction on a shape of wave functions etc. Acceptance of some restrictions entails some let even small “distortions” of electronic wave functions. And it, in turn, results in a divergence between the designed and experimentally measured values of those or other characteristics of a crystal or a molecule. To reduce a degree of a divergence with experiment it is necessary often to enter the empirical amendments. But implementation of these amendments results in disappearance of the essence the first-principle approach. Therefore the first-principle approach appeared successful at the description of “enough simple” systems - isolated atoms, ions [1].

For the decision of tasks of modeling of substance properties and processes occurring in substances is more acceptable proves semi-empirical approach, at which the physical equation is formed with the help of simple analytical functions. As a rule, the shape of these functions is set by the researcher from physical reasons, and parameters are found from conditions of concurrence of the designed and experimentally measured values of physical characteristics of researching substance. Last circumstance, certainly, results in smoothing of imperfections caused by shape of a physical equation. However the semi-empirical approach is not deprived contradictions. First of them consists that for description of properties of this or that substance are necessary the experimental data about the same sub-

stance. Therefore the opportunity of a prediction of before unknown compounds properties is lost already at the initial stage of researches. Besides, at the description of multicomponent compounds the definition of the big number parameters which are included in functions of interatomic interactions is necessary. It is obvious, that multicomponent connections represent the greater interest for research in view of them potentially the greater variety. But just for multicomponent compounds there are no reliable experimental data to which it would be possible to carry out binding of parameters. It is the second contradiction of the semi-empirical approach.

Owing to the above the development of methods which would be possess the advantages first-principle and semi-empirical methods and, whenever possible, be deprived their faults appear rather useful. One of ways of such decision is, that to experimental data to carry out the binding parameters of electronic distribution functions, instead of parameters of the functions describing interatomic interactions.

### **Statement of a problem**

At construction of model of the condensed matter it is necessary to lean on invariance, stationarity of those or other characteristics inherent in atoms, forming the substance. It is lawful to count these characteristics spatial configurations of electronic shells of atoms. Interacting with each other, atoms, similarly to building blocks form a building of a crystal lattice or chemical compounds. Knowing the configurations of electronic shells of atoms it is possible, basically, to explain, predict and program formation of chemical compounds, behavior of materials.

Unfortunately, now there are no experimental methods which with sufficient accuracy would allow carry out measurements of electronic density in atoms and compounds by methods of direct scanning. In this connection it is meaningful to take advantage of the data of "classical" experiment [2] for macroscopical samples. Link between experimental data and distributions of electronic density in atoms should become the theoretical treatments which are carried out in according with modern representations about a structure of a matter. The offered method is aimed at the description of the crystal stability and represents a version of a method of electronic density variation. Its theoretical substantiation is the Hohenberg and Kohn theorem [3] about an opportunity of representation of inner energy of multielectronic system as functional of electronic density. In contrast to quantum-mechanical methods function of distribution of electronic density is found not from a condition of a minimum of inner energy of a crystal or a molecule but from conditions of concurrence of the designed and experimentally measured values of characteristics of researched substances.

Thus approximately following scheme of actions is represented. It is necessary in the beginning to carry out comparison of configurations of crystal lattices or molecules of known substances and to find interrelation between a spatial "macroscopic" structure of these connections and a "microscopic" structure of electronic shells of atoms forming them. One of conditions of such interrelation is conformity of a crystal symmetry group to symmetry group of superposition of electronic shell densities of atoms. According to the carried out analysis the shape of functions of the distribution accompanying atoms must be construct. These functions, in turn, are used for drawing up of physical equation, describing state of substance. Then expressions for physical characteristics of a crystal or a molecule - interatomic distances, corners of interatomic bonds sublimation energies, elastic constants, frequencies of own vibration etc. can be received from the equation. These expressions are used then for the decision of back and direct tasks. The back task consists in definition of parameters of electronic density distributions on the basis of known experimental data. It is obvious, that at the decision of back task the data on unicomponent crystals and molecules first of all should be used. The direct task consists in definition of characteristics of crystals and molecules with the help of already constructed functions of distribution of electronic density.

Thus, as against to traditional semi-empirical approach when parameters of functions of interatomic interactions are determined for each concrete compound, here we receive a configuration of some “reference” atom understood in the sense that on a number of indexes its interaction with other “reference” atoms is the same as in real substance. Energy of interatomic interaction appears dependent on a relative disposition of atoms, what takes place in reality. The offered approach, in principle, allows give the description of enough complex multicomponent substances. As far as this description will be adequate to the validity depends on set of factors - legitimacy of starting assumptions of model, shapes of functions of electronic distributions and physical equation, accuracy of the decision etc.

### The description of model

In the present work the elementary variant of the offered procedure with elements of a covalent bond method is applied to the description of properties of metals and alloys. We shall consider model of the crystal lattice which is in an equilibrium condition in absence of external influences. As well as for any model, in the beginning it is necessary to enter simplifying assumptions:

- 1) Bond forces between a nucleus and own electronic shells of atom much stronger, than between atoms. The establishment of a nature of these forces is not a subject of the present research, but just these forces provide stationarity, an invariance of electronic shells of atom in various connections.
- 2) The bond between atoms in crystal or molecules is provided as owing to electrostatic interaction of their charging densities, and owing to repulsing of their electronic shells. The density of energy of mutual repulsing of electronic shells of interacting atoms is accepted proportional to product of their electronic densities.
- 3) The electronic density of isolated atom is described by spherical symmetrical function, centered on a nucleus and decreasing on infinity.

In aggregate these assumptions postulate approximation of the central and pair interactions. It is obvious, that symmetry group of superposition of spherical symmetrical distributions, centered on lattice knots is equivalent to symmetry group of a crystal.

Electronic density of atom we shall present as superposition of density of internal and external shells. Distribution of electronic density of an external shell we shall present as function normalized on a charge  $q$

$$\rho_e(R) = \frac{q\alpha}{4\pi^3 R R_m} [\exp(-\alpha^2(R - R_m)^2) - \exp(-\alpha^2(R + R_m)^2)] \quad (1)$$

where  $q$ ,  $\alpha$ ,  $R_m$  - parameters,  $R$  - distance from a nucleus. The maximal value of density  $\rho_e$  is reached approximately at  $R=R_m$ . The second item in square brackets (1) is entered that at  $R=0$  the electronic density  $\rho_e$  did not turn in infinity.

Distribution of internal shell density we shall present as Gauss function normalized on a charge  $(n-q)$

$$\rho_i = (n - q) \left( \frac{\beta}{\sqrt{\pi}} \right)^3 \exp(-\beta^2 R^2) \quad (2)$$

Where  $n$  - a charge of a nucleus,  $\beta$  - parameter of the distribution. Thus, the charge of a nucleus is compensated by charges of internal and external shells. At increase of the parameter  $R_m$  the charge of an external shell "leaves" from a nucleus, and the electronic configuration of atom becomes like to a configuration of an ion. At  $R_m=0$  external shell, as well as internal one, appear distributed in according with Gauss function (2), that is located on a nucleus. At  $\alpha \rightarrow 0$  superposition of electronic densities of external shells strive to uniform distribution, and at  $\alpha \rightarrow \infty$  external shells turn to the thin charged spheres of  $R_m$  radius.

At spherical symmetry of electronic shells of atoms the energy of electrostatic interaction of atoms 1 and 2 is the function dependent only from distance  $r$  between nucleus, and it is represented as coulombic interaction energy of charging densities of atom 1 with atom 2

$$\begin{aligned} \varphi_{12}^{es}(r) = & \varphi_{n1n2}^{es} + \varphi_{n1i2}^{es} + \varphi_{n1e2}^{es} + \varphi_{i1n2}^{es} + \\ & \varphi_{i1i2}^{es} + \varphi_{i1e2}^{es} + \varphi_{e1n2}^{es} + \varphi_{e1i2}^{es} + \varphi_{e1e2}^{es} \end{aligned} \quad (3)$$

Where  $\varphi_{n1n2}^{es}$  - energy of electrostatic interaction of nucleus,  $\varphi_{n1i2}^{es}$  - energy of interaction of a nucleus of atom 1 with an internal shell of atom 2, ...,  $\varphi_{e1e2}^{es}$  - energy of interaction of external shells.

The mutual repulsive energy  $\varphi_{12}^{rep}$  electronic environments of atoms 1 and 2 represents increase of kinetic, exchange etc. electronic energy as a result of shell overlapping. A primary factor of pushing away of electronic shells is, absolutely, Pauli principle. As well as in a case of coulombic interactions, this energy appears dependent on configurations of shells and on distance between nucleus. According to the second simplifying assumption expression for energy of mutual repulsing can be written as volumetric integral of overlapping

$$\varphi_{12}^{rep}(r) = s \int \rho_1(R) \rho_2(|\vec{R} - \vec{r}|) dV \quad (4)$$

Where  $\vec{R}$  - is the vector drawn from a nucleus of the first atom in a point of a space.  $\vec{r}$  - is vector, connecting the nucleus.  $s$  - is the area dimensional factor. Representation of repulsive energy as (4) allows to be limited to consideration only pair interactions. Thus, full energy of interaction of atoms 1 and 2 can be presented as the sum of electrostatic and repulsive energies.

$$\varphi_{12}(r) = \varphi_{12}^{es}(r) + \varphi_{12}^{rep}(r) \quad (5)$$

It is known, that coulombic forces are rather great. Therefore, in spite of the fact that atoms as a whole are electrical neutral, even the very insignificant redistribution of a charge in electronic shells can result in essential change of energy of interatomic interaction. At calculation of coulombic energy it necessary to add a great number close on values, but opposite on a sign numbers. That results in loss of accuracy. Reduction of calculations errors and essential increase of calculations speed can be achieved by application of analytical methods. For all integrals appearing in (3), (4), (5) the analytical shape was obtained and then it was used at calculations.

The inner energy of a crystal lattice in account on an elementary cell can be present as sum of pair interatomic interactions

$$U(a) = \frac{1}{2} \sum_{k,l} \varphi_{mn}(r_{kl}) \quad (6)$$

Here  $a$  - is a parameter of a lattice;  $m$  and  $n$  are sorts of the atoms which are disposed in knots  $k$  and  $l$  accordingly;  $r_{kl}$  - distance between atoms. For the ordered crystal one elementary cell is usually considered. Then index  $k$  - is a number of knot of a cell, and index  $l$  - is a number of knot disposed near  $k$ -st. Further, for simplification of the records and if it will not cause different interpretations, it is make sense do not write indexes  $m, n, k, l$  under the sum symbol. Then last ratio will be written down as

$$U(a) = \frac{1}{2} \sum_{k,l} \varphi(r) \quad (7)$$

Last equation should be considered as the physical equation of a crystal. From (7) the expressions for the major characteristics of a crystal can be received. The bond energy, by definition, is understood as a difference between inner energy of the whole and inner energy of its components. If the crystal components are free atoms, then bond energy value of a crystal can be found as value of its inner en-

ergy in an equilibrium condition. Currency [4] the positive value of bond energy is used. In particular, for a unicomponent crystal in calculation on one atom the bond energy  $E_B$  can be found from a ratio

$$E_B = -U(a_0) = -\frac{1}{2} \sum_l \varphi(r) \quad (8)$$

For a unicomponent crystal value of bond energy should coincide with value of energy of the sublimation taken with opposite sign.

$$E_B = E_S \quad (9)$$

Equilibrium value of a lattice parameter  $a_0$  is found from a condition of a minimum of inner energy

$$\frac{dU}{da_0} = 0 \quad (10)$$

Or, with the account (7)

$$\sum_{k,l} r \left( \frac{d\varphi}{dr} \right) = 0 \quad (11)$$

By definition [5], the module of bulk compression is

$$B = V_0 \frac{d^2U}{dV_0^2} \quad (12)$$

Where  $V_0$  – is researched equilibrium volume. For a crystal it is, as a rule, volume of an elementary cell. At all-round compression under action of insignificant pressure the elementary cell remains to similar itself, internuclear distances are proportional to parameter of a lattice, and the volume is proportional to a cube of a lattice parameter. In view of it from (12) and (7) it is possible to receive a ratio for the bulk module near to a condition of balance of a crystal.

$$B = \frac{1}{18V_0} \sum_{k,l} r^2 \frac{d^2\varphi}{dr^2} \quad (13)$$

The equations (8), (10), (13), written down for metal, form the system as a result of decision which three of five parameters  $\alpha$ ,  $\beta$ ,  $R_m$ ,  $q$ ,  $s$  can be found. Such ones were chosen  $\alpha$ ,  $R_m$ ,  $q$  - the parameters, describing a configuration of an external shell of considered atom. Parameters  $s$  and  $\beta$  are setting. Their values were selected according to two conditions. First, the designed dependence of inner energy on lattice parameter  $U(a)$  of considered unicomponent crystal should represent function with the only minimum in range from values  $a$  near to zero down to the values some exceeding equilibrium value  $a_0$ . Position and depth of this minimum should correspond to experimentally measured values of a lattice parameter  $a_0$  and energy of sublimation  $E_S$ . Second, the designed dependence of the module of all-round compression  $B(a)$  in the same range of definition should represent monotonously decreasing function. The parameter  $s$ , as against four others, characterizes a degree of repulsing of electronic shells of cooperating atoms, that is, is not connected to an electronic configuration of atom of a concrete element. Therefore  $s$  value should be identical to all elements.

According to the third simplifying assumption within the framework of the given model we can consider atoms only those elements which electronic shells are close to spherical symmetrical. Necessary (but not sufficient) attribute of spherical symmetrical of electronic shells of atoms is that the directions of interatomic bonds in crystals formed by considerable atoms are displayed in smallest degree. In other words, properties of the appropriate unicomponent crystals should be close to isotropic. Formally procedure of parameter definition of electronic distributions is applicable to crystals of any elements.

However last circumstance make force to exclude from consideration all nonmetals, semiconductors and, hence, such life-formed elements as carbon, nitrogen, oxygen. To elements most acceptable to consideration it is necessary to relate all, which crystallize in close-paced structures - FCC, HCP, and BCC. Those are majority of metals, inert gases. It is necessary to note, that the anisotropy of interatomic bonds in BCC structure is displayed in the greater degree, than in FCC or in HCP. The electronic configuration of hydrogen atom is spherical symmetrical. However the hydrogen here was not considered because of absence of data about its crystal lattice.

### Results and their discussion

The experimental data used for calculation about crystals of metals and inert gases are shown in table 1. Here and at calculations the out of system units – electron-volts and angstroms were used.

Table 1.

Initial experimental data [4, 5, 6] about crystals of some elements.

N of element	Chem. symbol	Name	Type of lattice	Lattice parameter $a_0/c_0, \text{Å}$	Sublimation energy, $E_s, \text{eV}$	Bulk module B, $\text{eV/Å}^3$
3	Li	Lithium	BCC	3.509	1,65	0.0724
4	Be	Beryllium	HCP	2.283/3.607	3.33	0.6261
10	Ne	Neon	FCC	4.430	0.02	0.0062
11	Na	Sodium	BCC	4.291	1.13	0.0424
12	Mg	Magnesium	HCP	3.2084/5.2104	1.53	0.2210
13	Al	Aluminium	FCC	4.049	3.34	0.4506
18	Ar	Argon	FCC	5.260	0.08	0.0100
19	K	Potassium	BCC	5,247	0.941	0.0200
20	Ca	Calcium	FCC	5.582	1.825	0.0948
21	Sc	Scandium	HCP	3.309/5,273	3.93	0.2715
22	Ti	Titanium	HCP	2.950/4.686	4.855	0.6561
23	V	Vanadium	BCC	3.028	5.30	1.0105
24	Cr	Chromium	BCC	2.885	4.10	1.1865
26	Fe	Iron	BCC	2.866	4.29	1.0504
27	Co	Cobalt	HCP	2.514/4.105	4.387	1.1948
28	Ni	Nickel	FCC	3.524	4.435	1.1609
29	Cu	Copper	FCC	3.615	3.50	0.8551
30	Zn	Zink	HCP	2.665/4.947	1.35	0.3733
36	Kr	Krypton	FCC	5.72	0.116	0.0112
37	Rb	Rubidium	BCC	5.70	0.850	0.0193
38	Sr	Strontium	HCP	6.085	1.696	0.0724
40	Zr	Zirconium	HCP	3.232/5.147	6.316	0.5200
41	Nb	Niobium	BCC	3.301	7.47	1.0623
42	Mo	Molibdenium	BCC	3.147	6.81	1.7008
44	Ru	Ruthenium	HCP	2.706/4.282	6.615	2.0025
45	Rh	Rhodium	FCC	3.803	5.752	1.6877
46	Pd	Palladium	FCC	3.889	3.936	1.1285
47	Ag	Silver	FCC	4.086	2.096	0.6285
48	Cd	Cadmium	HCP	2.973/5.607	1.16	0.2915
55	Cs	Cesium	BCC	6.140	0.827	0.0125
56	Ba	Barium	BCC	5.025	1.086	0.0643
58	Ce	Cerium	FCC	5.161	4.77	0.1492
59	Pr	Praseodmium	FCC	5.160	3.90	0.1910
70	Yb	Ytterbium	FCC	5.486	1.60	0.0830
72	Hf	Hafnium	HCP	3.195/5.057	6.35	0.6804

73	Ta	Tantalum	BCC	3.805	8.089	1.2483
74	W	Tungsten	BCC	3.165	8.66	2.0172
75	Re	Rhenium	HCP	2.761/4.458	8.10	2.3221
77	Ir	Iridium	FCC	3.839	6.93	2.2157
78	Pt	Platinum	FCC	3.923	5.852	1.7370
79	Au	Gold	FCC	4.079	3.78	1.0810
82	Pb	Lead	FCC	4.95	2.04	0.2684
90	Th	Thorium	FCC	5.084	5.926	0.3389

It follows from the given model that the electronic density of atom and, hence, interatomic potential are the functions decreasing until infinitive distances. However at numerical calculations it is necessary to limit the radius of atomic interaction. At calculation of the lattice sums in FCC and BCC structures the interactions down to the twelfth coordination sphere were taken into account. In HCP structure 20 coordination spheres were considered, that by quantity of internatomic bonds approximately corresponds to twelve spheres in cubic structures. However, the parameter values of electronic distributions functions change insignificantly at consideration of six or more coordination spheres.

During a variation of electronic density parameters with the purpose of their definition it was established, that value  $s=0,55\text{\AA}^2$  appears the most acceptable. It means, that at such  $s$  value for each of the unicomponent crystals shown in table 1, it is possible to find such four of numbers ( $\beta$ ,  $\alpha$ ,  $R_m$ ,  $q$ ), describing distribution of own electronic density of atom, that at the made assumptions and put forward requirements to dependences  $U(a)$  and  $B(a)$  the designed equilibrium characteristics of crystals will coincide with experimentally observably, shown in table 1. The increase of  $s$  value more than on 10 % in comparison with  $0,55\text{\AA}^2$  results to that for some crystals on dependence  $U(a)$  at all it is not possible to receive a minimum appropriate to an equilibrium condition of a crystal. Reduction  $s$  more than on 10% results in occurrence on the given dependence additional minimum at  $a$  value much less then  $a_0$ . It is possible that its deep appears more then experimental one -  $E_B$ . The reason of occurrence of this collateral minimum is prevailing action of coulombic forces at artificial supported distribution of electronic density.

Thus, for the description of electronic density distribution of own shells of atom it is necessary to define four parameters -  $\beta$ ,  $\alpha$ ,  $R_m$ ,  $q$  from three equations (8), (10), (13). In this sense arbitrariness in a  $\beta$  choice nevertheless remains. Actually, at imposing of the above mentioned conditions on dependence of inner energy and the bulk module on a lattice parameter arbitrariness in a choice of  $\beta$  appears insignificant ~1% from the value shown in table 2. For alkaline, alkaline-land metals, beryllium and lead it is not possible to receive monotonously decreasing dependence  $B(a)$  in all range of definition. The designed values of parameters  $\beta$ ,  $\alpha$ ,  $R_m$ ,  $q$  for atoms of various elements are given in table 2.

Table 2.

The designed values of electronic distributions parameters of some elements

N of element	Chem. symbol	$\beta, \text{\AA}^{-1}$	$\alpha, \text{\AA}^{-1}$	$q, e$	$R_m, \text{\AA}$	$r_l, \text{\AA}$
3	Li	2.764173	0.546936	0.945280	2.635191	3.039
4	Be	1.731056	1.104678	0.897093	2.129364	2.283
10	Ne	2.585808	1.331289	0.241844	2.635617	3.132
11	Na	2.879620	0.997390	0.759334	3.441605	3.716
12	Mg	2.842538	0.968978	1.202448	2.461944	3.208
13	Al	2.444923	0.900809	1.366452	2.393981	2.862
18	Ar	2.527302	1.071491	0.236544	3.448049	3.719
19	K	2.808297	1.213018	0.699993	4.222663	4.544
20	Ca	3.040230	0.784774	1.269872	3.058856	3.945
21	Sc	2.598972	0.770736	1.543753	2.751772	3.309
22	Ti	2.474576	0.999417	1.537389	2.565215	2.950
23	V	2.364314	1.148880	1.284725	2.555139	2.622

24	Cr	2.381445	1.243625	1.152249	2.414736	2.498
26	Fe	2.288450	1.240741	0.864903	2.549952	2.482
27	Co	2.347653	1.117174	1.232924	2.285457	2.514
28	Ni	2.295489	1.235256	0.898480	2.432103	2.491
29	Cu	2.347242	1.109497	1.003367	2.389273	2.556
30	Zn	2.439024	1.133795	0.785830	2.528043	2.665
36	Kr	2.521849	0.990791	0.330732	3.694637	4.044
37	Rb	2.674043	1.418261	0.710332	4.601301	4.936
38	Sr	2.788917	0.836909	1.246030	3.356441	4.302
40	Zr	2.475248	0.921224	1.646757	2.952902	3.232
41	Nb	2.455619	1.046181	1.776995	2.700969	2.859
42	Mo	2.517078	1.152556	2.242617	2.368049	2.725
44	Ru	2.420547	1.250684	1.514218	2.498619	2.706
45	Rh	2.389548	1.243086	1.274950	2.556324	2.708
46	Pd	2.400054	1.229059	1.013934	2.639279	2.750
47	Ag	2.450473	0.881641	1.637625	2.264881	2.889
48	Cd	2.522619	1.155664	1.031654	2.733403	2.973
55	Cs	2.670480	0.760571	0.814255	4.563679	5.317
56	Ba	2.746004	0.561780	1.547170	3.111520	4.351
58	Ce	2.507277	0.576070	1.664465	3.222022	3.649
59	Pr	2.494059	0.815739	1.354816	3.412347	3.648
70	Yb	2.603638	1.198876	1.233204	3.449819	3.879
72	Hf	2.456810	0.882982	1.791531	2.822318	3.195
73	Ta	2.670529	1.092981	3.165174	2.626432	3.295
74	W	2.448038	1.079056	2.053776	2.557841	2.741
75	Re	2.433989	1.113561	1.905437	2.495681	2.761
77	Ir	2.412894	1.158950	1.500306	2.547326	2.714
78	Pt	2.400883	1.176469	1.214281	2.665379	2.774
79	Au	2.444277	1.069955	1.354943	2.628503	2.884
82	Pb	2.571297	1.170315	1.519206	3.053763	3.499
90	Th	2.475708	0.808318	1.694699	3.330278	3.594

Apparently from the table, that on the order of value each parameter appears identical to all elements. In particular, the value of a charge of external shells appears comparable to an elementary charge. The least it appears for atoms of inert gases - Ne – 0.241e, Ar – 0.237e.  $\beta$  values for the majority of elements are close to 2.5. It means that internal shells in various atoms are spread approximately in a similar shape. External shells are spread in space in the greater degree in comparison with internal ones to what smaller  $\alpha$  values testify in comparison with  $\beta$ . The radius of the maximal density of external shell  $R_m$  is comparable with radius of the first coordination sphere  $r_1$  and as a rule,  $R_m < r_1$ . For comparison the values of the nearest internuclear distances  $r_1$  are resulted in the last column of table 2. As example the calculated dependences of inner energy and bulk module for nickel are shown at fig. 1. It can see from figures, the put forward requirements to these functions are executed. The scheme of the mutual overlapping from two nickel atoms which are on the minimal internuclear distance in the nickel crystal is shown on fig. 2.



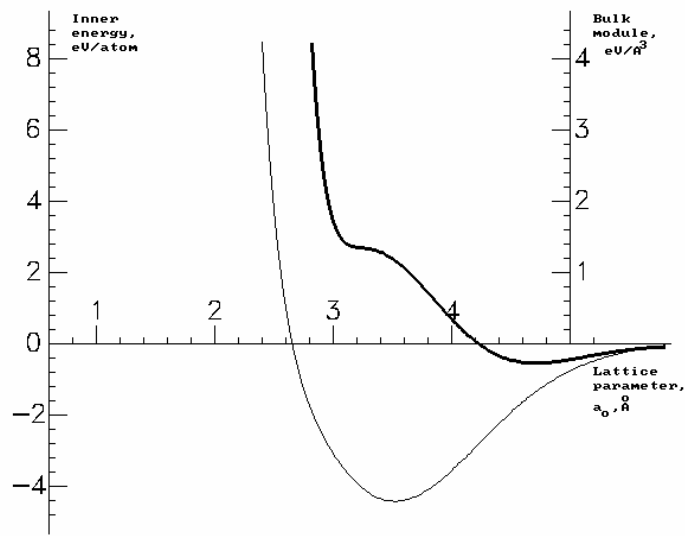


Fig. 1. Calculated dependence of inner energy (thin line) and bulk modulus (bold line) on lattice parameter of nickel.

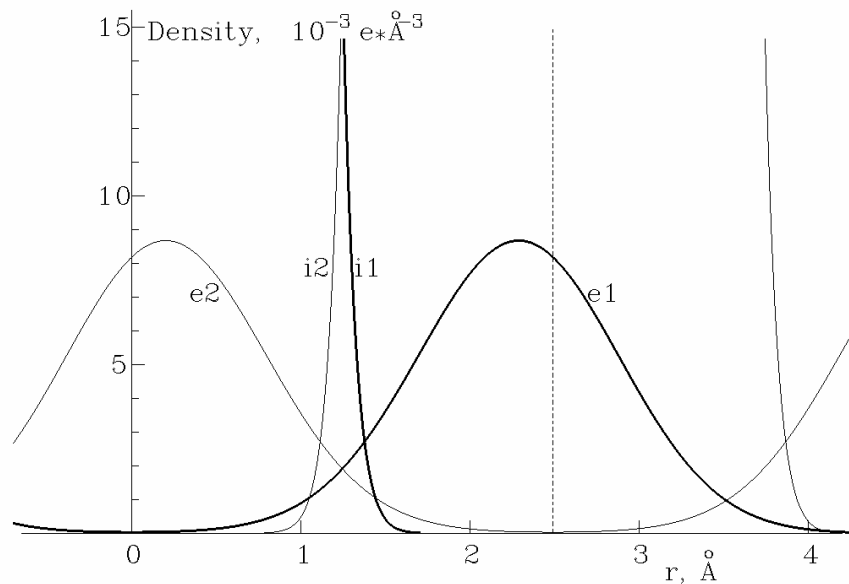


Fig.2. Distribution of electronic density components from two neighboring atoms in nickel crystal. The nucleus of the first atom is in the beginning of the coordinates. The position of the second atom is marked by dotted line. i1 and i2 are densities of internal shells. e1 and e2 are densities of external shells.

From data of tables and the diagram follows, that for the majority of metals the model predicts so deep mutual penetrations of electronic shells of atoms at crystal formation, that the nucleus of each atom appears located near to a maximum of electronic densities of the external shells from the neighboring atoms. It results to that knots of a crystal lattice (and, hence, nucleus of atoms) appear located in the positions of local maxima of electronic density created by external electronic shells of atoms of the first coordination sphere. The value of this local maximum is easy to estimate from data of the diagram. It is necessary for this purpose only the maximal value of external shell density to multiply by number of knots of the first coordination sphere.

$$\rho_{\max} \approx z_1 * \max \rho_e \approx 0,1e / \overset{o}{A}^3 \quad (13)$$

It approximately in 600 times is less than maximum of electronic density of the internal shell, making  $\sim 60e/\overset{o}{A}^3$ . As the internal shells are located on nucleus, in crystal the maximum positions of internal and external shells coincide and are in knots of a lattice. Such configuration is quite explained from the point of view of the electrostatic. Energy of interaction of pair atoms and, hence, inner energy appear rather sensitive to a spreading degree as internal and external shells. Therefore it is quite inadmissible to neglect by spreading of internal shells that is to assume, that part of electrons is "in a nucleus".

Criterion of applicability of the offered model to the description of behavior of alloy crystals should become a degree of conformity of their designed and experimentally observably characteristics. In present work the binary alloys with B2 superstructure were researched. Such choice is dictated, first, by that despite of a much more share of application of multicomponent alloys in mechanical engineering, in the literature does not contain almost data on properties of multicomponent crystals. Therefore comparison of the designed and experimental characteristics can be carried out only for binary alloys. Second, the greatest divergence with experimental data should be observed for the alloys having the greatest deviation from composition of pure metal. In case of a binary alloy it is equiatomic composition AB, corresponding to B2 superstructure. Thirdly, the knots of B2 superstructure form the BCC lattice, which is more "friable" in comparison with FCC and HCP. In stability formation of superstructures on basis of BCC lattice an essential role should play "unsphericity" of electronic shells of atoms. Therefore successful application of the model to BCC alloys would allow hope at the same relatively alloys of close-paced structures. And, at last, fourthly, superstructure B2 is one of the most investigated, about what testify presence in the literature the experimental data about B2 alloys [7, 8]

The most accessible and authentic are the diffractometrical data about structure of a crystal and the sizes of its elementary cells.

Stability of connection or crystal lattice of an alloy is provided also with that the absolute value of bond energy in calculation on an elementary cell must be more then sum of sublimations energies of the metals forming a cell on the value of alloying heat  $H_{all}$ .

$$E_B = |U_0| = \sum_k E_{Sk} + H_{all} \quad (14)$$

where summation is carried out on atoms of a cell. The measurements executed for number of alloys [6] shown, that the value of heat alloying heat makes  $\sim 5\%$  from the sum of sublimation energies. Therefore

$$E_B \sim 1,05 \sum_k E_{Sk} \quad (15)$$

Apparently, on the same ratio it is necessary to orient for alloy AB with B2 superstructure.

$$E_B \sim 1,05(E_{SA} + E_{SB}) \quad (16)$$

Experimental measurements of elastic modules for the majority of alloys are not executed. The main reason of it is difficulty of manufacturing of enough large monocrystal samples of the given composition and superstructure. Therefore comparison of the designed values of elastic modules of an alloy can be carried out only with the appropriate data for metals.

Formal calculations of the lattice parameter, bond energy and the bulk module are carried out for everything found in the literature alloys with B2 superstructure. At this point any arguments were not considered for the benefit of that this or that one or another alloy would be excluded from consideration. Results of calculations and the appropriate experimental data are shown in table 3.

Table 3.

The designed and experimental values of a lattice parameter [7, 8], bond energy [6] and the bulk modulus for alloys with B2 superstructure.

Alloy	$a_0, \text{\AA}$ calculation	$a_0, \text{\AA}$ experiment	$E_B, eV/cell$ calculation	$(E_{SA}+E_{SB}), eV$ experiment	$B, eV/\text{\AA}^3$ calculation
AgCd	3.409	3.333	3.899	4.12	0.4154
AgCe	3.721	3.74	6.743	7.73	0.1668
AgLi	3.366	3.167	3.903	4.61	0.1811
AgMg	3.380	3.32	4.417	4.49	0.3876
AgPr	3.888	3.735	5.836	6.86	0.1772
AgSc	3.519	3.412	6.71	6.89	0.3534
AgZn	3.140	3.155	4.482	4.31	0.5218
AlCo	2.995	2.85	7.223	7.35	0.6685
AlLi	3.267	3.776	4.394	4.99	0.1914
AlMg	3.376	3.32	4.6508	4.87	0.3297
AlFe	2.966	2.90	7.568	7.63	0.6794
AlIr	3.057	2.977	8.990	10.27	1.0292
AlNa	3.948	3.73	3.207	4.47	0.1056
AlNi	2.920	2.887	7.529	7.77	0.7201
AlPd	3.093	3.03	6.86	7.28	0.6849
AlPr	3.742	3.82	6.145	7.24	0.1603
AlRh	3.042	2.99	8.593	9.09	0.8798
AlRu	3.054	3.03	8.935	9.96	0.9182
AuCd	3.308	3.33	4.513	4.94	0.6192
AuCe	3.578	3.70	7.089	8.55	0.2134
AuCs	5.256	4.263	2.071	4.61	0.0474
AuMg	3.317	3.26	4.400	5.31	0.4267
AuPr	3.746	3.68	6.057	7.68	0.1517
AuZn	3.119	3.12	4.920	5.13	0.7454
AuSc	3.477	3.37	6.871	7.71	0.3667
BaZn	3.401	4.09	2.689	3.21	0.0936
BeCo	2.712	2.611	7.605	7.72	1.1097
BeCu	2.725	2.701	6.595	6.83	0.9226
BeNi	2.687	2.610	7.470	7.765	1.1159
BePd	2.866	2.819	6.383	7.266	0.8338
CdCe	3.668	3.861	5.839	5.93	0.2012
CdLi	3.535	3.366	2.9285	2.81	0.1172
CdPr	3.730	3.828	4.780	5.06	0.1553
CdSc	3.610	3.513	4.915	5.09	0.2389
CeMg	3.678	3.875	6.084	6.30	0.1857
CeZn	3.458	3.72	5.755	6.12	0.2003
CoFe	2.817	2.85	8.788	8.68	1.1267
CoSc	3,282	3,145	6,885	8,32	0,3410
CoTi	3,057	2,99	8,857	9,24	0,7939
CoZr	3,246	3,197	9,387	10,703	0,4870
CuSc	3,276	3,25	6,61	7,43	0,3371
CuPd	2,961	2,96	7,261	7,44	1,0010
CuZn	2,956	2,94	4,515	4,85	0,6058
FeRh	2,914	2,987	10,457	10,04	1,4570
FeTi	3,021	2,976	9,293	9,14	0,8390
IrSc	3,313	3,206	8,332	10,86	0,4601

IrTi	3,115	3,11	10,964	11,785	1,1707
LiTi	3,255	3,48	5,524	6,51	0,2676
LiPb	3,872	3,52	3,986	3,69	0,1094
MgPb	3,980	3,12	3,514	3,57	0,1412
MgPd	3,191	3,12	4,553	5,47	0,4438
MgPr	3,791	3,88	4,944	5,43	0,1410
NiSc	3,153	3,15	7,174	8,36	0,3706
NiTi	2,985	3,013	9,228	9,29	0,8676
NiZn	2,887	2,914	5,261	5,79	0,7599
PdSc	3,313	3,283	6,929	7,87	0,3914
PrZn	3,607	3,67	4,586	5,25	0,1239
PtSc	3,304	3,270	8,021	9,78	0,5010
PtZr	3,305	3,31	11,082	12,17	0,7713
RhSc	3,258	3,206	8,117	9,68	0,4467
RhZr	3,239	3,260	11,086	12,07	0,7030
RuSc	3,288	3,203	8,248	10,55	0,4182
RuTi	3,102	3,06	10,703	11,47	1,0355
RuV	2,995	2,996	11,725	11,91	1,4279
RuZr	3,241	3,25	11,270	12,93	0,6882

The major characteristic here, certainly, is the lattice parameter. The greatest divergences between the designed and experimental values  $a_0$  are observed for alloys of alkaline and alkaline land metals AlLi, AlNa, AuCs, BaZn, CdLi, LiTi. For alloys of scandium, cerium, praseodim deviations take place in a lesser degree. To alloys of transitive metals a correlation between  $a_{0calc}$  and  $a_{0exp}$  are quite acceptable.

In values of bond energy the greater degree of a divergence take place. For the majority of connections the designed values of bond energy just not exceed the total energy of sublimations of metals – components of an alloy. And the worse results are observed again for alloys of alkaline and alkaline lands metals.

Designed values of the bulk module for alloys are comparable to the appropriate experimental data for metals (tabl. 1.).

The scheme of mutual overlapping of electronic densities from two nearest atoms Ni and Al in alloy NiAl is shown on fig. 2.

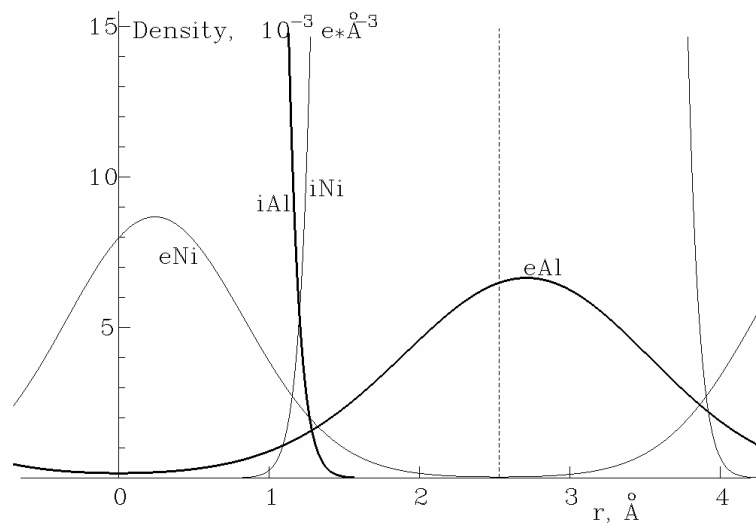


Fig.3. Distribution of electronic density components from two neighboring atoms in AlNi crystal. The nucleus of the aluminium atom is in the beginning of the coordinates. The position of the nickel atom is marked by dotted line. iAl and iNi are densities of internal shells. eAl and eNi are densities of external shells.

Here, as against fig. 2, nickel atoms are appeared in positions of more spreading maxima of electronic density created by external shell of the neighboring aluminium atoms.

Dependence of interaction energies of atoms Ni and Al in alloy NiAl is submitted on fig. 3. It is typical, that as against to traditionally used empirical potentials with alone minimum on the submitted diagram takes place not only a deep minimum, but also an insignificant positive maximum.

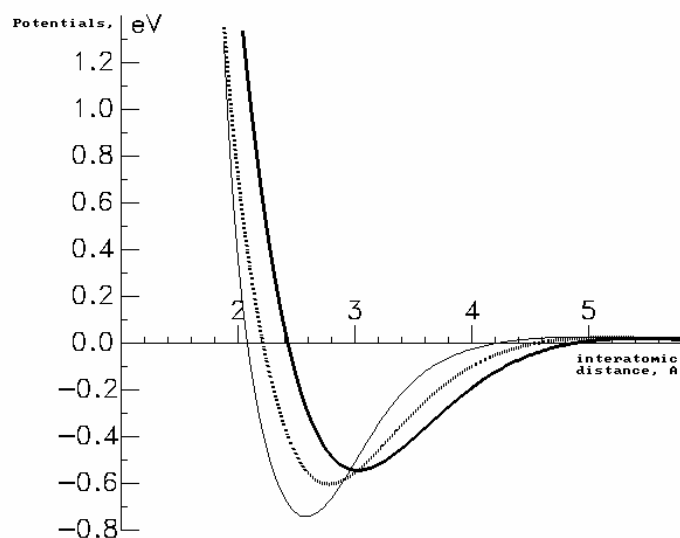


Fig. 1. Dependence of potentials of interatomic interaction on distance between atoms in AlNi alloy. Al-Al – bold line. Ni-Ni – thin line. Al-Ni – dotted line.

Certainly, that the model of the central pair interatomic potentials can not describe all properties of crystals, for example infringement of Cauchy relations. Nevertheless, it is possible to try explain the reasons of crystallization of various elements in quite certain structures - FCC, BCC, HCP. For this

purpose to atom should assign not one but several external electronic shells, each of which is distributed in according with (1).

Then the most stable state of a crystal lattice will be reached when nucleus appear in the positions of density maxima created not only the first, but also the subsequent shells of neighbors. Such configuration can arise only in the event if the radius of first shell  $R_{m1}$  is close to radius of the first coordination sphere, the radius of the second shell is close to radius of the second sphere etc. It means, that, a sequence radius relation of shells  $R_{mj}/R_{m1}$  for elements, crystallizing in FCC lattice should be close to: 1; 1,414; 1,732; 2; for HCP elements: 1; 1,414; 1,633; 1,732; for BCC elements: 1; 1,154; 1,633; 1,915. That is, the structure of a crystal should be displayed owing to interaction of each atom with the environment in radius not less than radius of the third coordination sphere. In a case, for example, small cluster ( $\sim 10 \text{ \AA}$ ) for the majority of its atoms of such environment is absent. Therefore the structure small cluster should differ from structure of a volumetric crystal. It is obviously that for construction of multi-shell model of atom the attraction of greater number of experimental data and, probably, execution of additional special measurements will be necessary.

Thus, the offered model with a sufficient degree of adequacy allows to describe atomic interactions of atoms in crystals of alloys of simple and transitive metals and, hence, a number of properties of these crystals. In particular, the model is applicable to calculation of elastic characteristics, the description of processes of elastic and plastic deformation, description of lattice state near defects, etc.

At the same time, because of discrepancy of bond energies the model does not allow to predict a stable state of an alloy of given composition. Apparently, it should search the reasons of detrimentation of the model in the made above simplifying assumptions. Gradual refusal of them should result in expansion of a class of adequately described substances. First of all, simulation of electronic shell density by unspherical functions will allow to give the quantitative description of atomic interactions oxides, carbides, silicides, nitrides, molecules of alive systems etc. Approach of pair overlapping of shells (4) also demands the further overestimation. At this point, most likely, it is inadmissible to be limited only by threefold, fourfold or higher order interactions. It is necessary to take into account overlapping of electronic densities from all atoms of considered connection. The assumption about stationary of electronic shells is the main reason of that is impossible to reach experimentally observable minimum of bond energy of an alloy.

Basically the specified imperfections of model are eliminated and will be a subject of the further consideration. The main result of the carried out research is development of a technique of direct and back tasks decision, which allow connect the electronic configuration of atom and crystal properties.

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