CELLULAR APPROXIMATION OF THE METHOD OF THE MODEL
ELECTRON DENSITY FUNCTIONAL.
ALLOYS OF ALKALI METALS

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The expression obtained in Part 1 of this work for the total energy of a disordered binary substitution alloy is employed to calculate the thermodynamic characteristics of alloys of the systems Na-Rb, Na-Cs, Li-Na, Li-K, K-Rb, Rb-Cs, K-Cs, Na-K. A model expression, whose parameters are calculated starting from the equilibrium characteristics of the metals studied, is employed to describe the energy of interaction of ions with conduction electrons. In order to calculate the properties of alloys no additional parameters are introduced into the theory, but rather the values of the parameters of the pure components are employed.

In [1] we derived an expression for the total energy \( E[p] \) of a metal and disordered binary substitution alloy in the cellular approximation of the model electron density functional method. The existing expressions of the theory of the electron density functional are employed to give the self-energies of the characteristic and almost-free electrons. The unknown quantity of the proposed method is the dependence of the average value of the ionic pseudopotential over the Wigner-Seitz (WS) cell for each type of atom on the value of the average density of almost-free electrons and the volume of the cell. Since the same expressions are employed for \( E[p] \) for both the pure metal and the alloy, this dependence can be found from the equilibrium thermodynamic properties of pure metals. In this connection there arises the question of choosing the optimal set of equilibrium properties of metals which have the greatest effect on the energy of formation \( \Delta H \) of the alloy and the elastic properties of the alloy. To solve this question we shall study a disordered alloy, consisting of simple metals, in which the interaction between the core electrons of neighboring atoms can be neglected, i.e., \( E_i[p_C] = 0 \) (the formula (1) of [1]). We represent the density within each sphere in the form
\( \rho_\alpha (r, \Omega) = \rho_\alpha (r, \Omega) + \Delta \rho_\alpha (r, \Omega), \)  

(1)

where \( \rho_\alpha (r, \Omega) \) is the density of almost-free electrons in a WS cell of the pure metal of type \( \alpha \). It is obvious that the charge transfer \( \Delta n_\alpha \) in the alloy into a WS cell occupied by an atom of type \( \alpha \) is equal to

\[ \Delta n_\alpha = \int \frac{1}{2} \Delta \rho_\alpha (r, \Omega) \, dV \]

(2)

and the condition of electric neutrality (11) from [1] is satisfied. For a disordered alloy, in the absence of short-range order in the arrangement of the atoms, the Coulomb interaction between the WS cells is equal to zero.

Substituting Eq. (1) into the expression for the total energy (the formula (1) of [1]) and expanding it up to second order in \( \Delta \rho_\alpha (r) \) we obtain

\[ E = \sum \frac{c_\alpha}{2} \left[ E_\alpha (\Omega) + \frac{1}{2} \frac{\partial^2 E_\alpha}{\partial \Delta n_{\alpha}^2} \right] + \sum \frac{c_\alpha}{2} \left[ \frac{\partial^2 E_\alpha}{\partial \Delta n_{\alpha}^2} \right], \]

(3)

where \( E_\alpha (\Omega) \) and \( \mu_\alpha (\Omega) \) are the energy and chemical potential of the electrons of the pure metal \( \alpha \) and \( \Omega \) is the volume of the alloy; \( c_\alpha \) is the concentration of atoms of type \( \alpha \) in the alloy. The contribution to the total energy of the alloy in second order in \( \Delta \rho_\alpha (r, \Omega) \) depends on the form of \( \Delta \rho_\alpha (r, \Omega) \). The last term in Eq. (3) describes the nonlinear dependence of the energy of a WS-cell occupied by an atom of type \( \alpha \) on the change in the number of almost-free electrons \( \Delta n_\alpha \) in a cell, and the quantity \( \frac{\partial^2 E_\alpha}{\partial (\Delta n_{\alpha})^2} \) is always positive and characterizes the rate of change of the chemical potential \( \mu_\alpha (\Omega) \) as \( \Delta n_\alpha \) increases. If it is assumed that the density of the transferred charge \( \Delta \rho_\alpha (r, \Omega) \) is constant over the volume of a WS cell \( \Delta \rho_\alpha = \Delta n_\alpha /\Omega \), then the last term in Eq. (3) can be represented in the form

\[ \frac{\partial^2 E_\alpha}{\partial (\Delta n_{\alpha})^2} \frac{1}{\Omega} \left[ \int \frac{dV \cdot dV'}{r - r'} \right] \]

(4)

From the condition that the energy (3) is minimum with respect to the charge transfer \( \Delta n_\alpha \) and the condition of electric neutrality (11) from [1] it is easy to obtain the charge \( \Delta n_\alpha \) transferred into the WS cell occupied by an atom of type \( \alpha \) and the energy of formation of the disordered binary alloy \( \Delta H \)

\[ \Delta n_\alpha = \frac{\mu_B (\Omega) - \mu_A (\Omega)}{c_B \frac{\partial^2 E_B}{\partial (\Delta n_{\alpha})^2} + c_A \frac{\partial^2 E_A}{\partial (\Delta n_{\alpha})^2}}, \]

(5)

\[ \Delta H = E (\Omega, \Delta n_\alpha) - c_A E_A (\Omega_A) - c_B E_B (\Omega_B) = \sum \frac{c_\alpha}{2} \left[ E_\alpha (\Omega) - E_\alpha (\Omega) \right] - \frac{1}{2} \frac{c_A c_B}{\left| \frac{\partial^2 E_A}{\partial (\Delta n_{\alpha})^2} + \frac{\partial^2 E_B}{\partial (\Delta n_{\alpha})^2} \right|}, \]

(6)

where \( \Omega_A \) and \( \Omega_B \) are the equilibrium volumes of the pure metals, respectively.

The expression (6) leads to two conclusions. First, starting in second order in \( \Delta \rho_\alpha (r, \Omega), \Delta H \) depends on the specific form of the redistribution of the electron density \( \Delta \rho_\alpha (r, \Omega) \). This is why \( \Delta H \) depends weakly on the form of \( \Delta \rho_\alpha (r, \Omega) \) in the method of the model electron density functional (MEDF) [2, 3]. Second, \( \Delta H \) is determined by the difference of the chemical potentials of the pure metals and their elastic properties. The explicit dependence of the energy of formation of the alloy on the bulk modulus and the equilibrium volume follows from the fact that in second order in \( (\Omega - \Omega_\alpha) \)

\[ E_\alpha (\Omega) - E_\alpha (\Omega_\alpha) = \frac{1}{2} \frac{B_\alpha}{\Omega_\alpha} (\Omega - \Omega_\alpha)^2, \]

(7)

where \( B_\alpha \) is the bulk modulus of the metal \( \alpha \). The first term in (6) is always positive and increases as the bulk modulus and the difference of the equilibrium volumes of the pure components increase; this impedes alloy formation. The second term in (6) is always negative and gives rise to alloy formation. This corresponds to the first two Yum-Rozental rules of alloy formation [4].