Calculation of ordering energies by the model potential method taking into account the linear size effect in the Ni-14at.%Pt alloy

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Abstract. For disordered binary solid solutions, a new method is proposed for calculating the ordering energies in an arbitrary coordination sphere, taking into account the linear size effect. Using the model potential of transition metals, the Animalu calculated the ordering energies of the Ni-14at.%Pt solid solution in twelve coordination spheres. The temperature of the order-disorder phase transition was estimated for the Ni-14at.%Pt alloy. Satisfactory agreement with the experimental data is obtained.

Keywords: binary alloys, ordering energy, short-range order parameters, pseudopotential method.

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coordination spheres, taking into account the static displacements of atoms due to the size effect.

The aim of this work is to develop a method for calculating the ordering energies in binary alloys based on [5] in an arbitrary coordination sphere taking into account the linear size effect and to perform such a calculation using the example of a disordered Ni-14at.%Pt solid solution.

2. ACCOUNT OF STATIC DISPLACEMENTS IN THE ELECTRONIC THEORY OF CLOSE ORDER

As shown in [5], the configurational energy of a disordered solid solution in the presence of static atomic displacements due to the size effect can be written as:

\[ E_{\text{conf}} = A_0 - B_0 + C_A C_B \sum_{i=0}^{C_i} C_i \alpha_i V(r_i), \]

where

\[ V(r_i) = \left[ A(r_i) - B(r_i) \right]. \]

In this expression, the function \( A(r) \) is the fraction of the ordering energy recorded without taking into account the size effect:

\[ A(r_i) = V_{11}^{AA}(r_i) + V_{11}^{BB}(r_i) - 2V_{11}^{AB}(r_i) \]

and \( B(r) \), taking into account the linear size effect, \( \alpha_i \) is the short-range order parameter on the \( i \)th coordination sphere of radius \( r_i \), \( C_i \) is the coordination number, \( C_A \) and \( C_B \) are the component concentrations.

The energy of pair interaction of atoms of type \( A \) entering into formula (2) is written using the normalized characteristic function \( G_{AA}(q) \), which includes the contributions of electrostatic interaction and second-order perturbation theory:

\[ V_{11}^{AA}(r_i) = \frac{2\left(Z_A^*\right)}{\pi} \int G_{AA}(q) \frac{\sin qr_i}{qr_i} dq, \]

The contribution to the ordering energy due to the linear size effect can also be written using normalized characteristic functions in the form [5]:

\[ \Delta_{\text{size}} = -\Delta_{\text{AA}} \left[ V_{21}^{AA}(r_i) - V_{21}^{BB}(r_i) \right] - \Delta_{\text{AB}} \left[ V_{11}^{BB}(r_i) - V_{11}^{AB}(r_i) \right]. \]

The functions \( V_{21}^{BB}(r_i) \) and \( V_{21}^{AB}(r_i) \) are defined similarly.

In this work, in calculating the ordering energies, we used form factors of the model potential of transition metals of Animalu, which have the form [6]:

\[ W_{\text{bare}}(q) = W_{\text{ext}}(\mathbf{k}_F, \mathbf{q} + \mathbf{\phi}) + B(q), \]

\[ B(q) = -\frac{F_{ij}}{z_{ij}} \left[ 2\pi Z A_i \left| q_r \right| \right] \cos(q R_m \cos(q R_m) + \frac{\Delta q}{\Omega_{ij}}) \times \left[ \sin(q R_m) - q R_m \cos(q R_m) \right]. \]

For \( F_{ij} = \mathbf{F} \) we get:

\[ F(\mathbf{k}_F, \mathbf{q} + \mathbf{\phi}) = -\frac{4\pi R_m^3}{\Omega_0} \sum_{l} (2l + 1) \times \times \left( A_l - C_l \left[ j_l^2(x) - j_{l-1}(x) j_{l+1}(x) \right] \right) R_l(\cos \theta). \]

For \( F(\mathbf{k}_F, \mathbf{q} + \mathbf{\phi}) \) we get:

\[ F(\mathbf{k}_F, \mathbf{q} + \mathbf{\phi}) = -\frac{8\pi R_m^3}{\Omega_0 \left( x^2 - y^2 \right)} \sum_{l} (2l + 1) \times \times \left[ y_{l+1}(x) j_l(y) - y_{l-1}(x) j_{l+1}(x) \right] P_l(\cos \theta'), \]

where
\[ x = k_F R_m, \quad y = |\vec{k}_F - \vec{q}| R_m, \quad C = \frac{Z}{R_m}, \]

\[ \cos \theta = \left(1 - \frac{q^2}{2k_F^2}\right), \quad \cos \theta' = \frac{x^2 + y^2 - (qR_m)^2}{2xy}, \]

\( j \) are the Bessel spherical functions, \( R_\theta \cos \theta \) are the Legendre polynomials, \( \Omega_0 \) is the atomic volume,

\[ \varepsilon(q) = 1 + \left[1 - f(q)\right] \frac{4\pi Z e^2}{\Omega_0 q^2} \left(\frac{2}{3} E_F\right)^{-1} \times \]

\[ \frac{1}{2} + \frac{4k_F^2 - q^2}{8k_F q} \ln \left(\frac{2k_F + q}{2k_F - q}\right), \]

\[ E_F = \frac{\hbar^2 k_F^2}{2m^*}, \quad k_F \) is the Fermi momentum, \( m^* \) is the effective mass of the electron, \( e^2 = (1 + \alpha_{\text{eff}}) e^2 \), and \( f(q) \) is the correction for the exchange and correlation of electrons. In the work, the function proposed by Hubbard and Sham was used.

\[ f(q) = \frac{q^2}{2\left(q^2 + k_F^2 + k_s^2\right)}, \quad k_s = \frac{2k_F}{\pi}. \]

The used parameter values of the nickel and platinum pseudopotentials are given in Table 1.

The temperature correction was introduced by multiplying the form factors of nickel and platinum by the factors \( \exp(-M) \), where

\[ M = \frac{q^2}{2} \left\langle u_i^2 \right\rangle = \frac{q^2}{2} \frac{3\hbar^2 T}{2Mk_B\Theta_D} \left(\Phi(X) + \frac{X}{4}\right), \]

\( \left\langle u_i^2 \right\rangle \) are the mean square displacements, \( \hbar \) is the Planck constant, \( T \) is the temperature, \( M \) is the mass of the atom, \( k_F \) is the Fermi constant, \( \Theta_D \) is the Debye temperature, \( \Phi(X) \) is the Debye function, \( X = \Theta_D/T \). The calculations were carried out for a temperature of 1000°C.

### 3. METHOD FOR CALCULATING THE STATIC DISPLACEMENT PARAMETERS

The parameters of the static displacements \( \Delta_{AA,i} \) and \( \Delta_{BB,i} \) were calculated using the scheme for changing the sizes of nickel and platinum atoms during the formation of a solid solution, which is shown in Fig. 1 and is similar to the scheme used in [7]. It is assumed that the dependences of atom sizes on concentration are close to linear and parallel to each other. In Fig. 1, these dependences are shown by solid lines. Let \( r_{AA,i}^0 \) and \( r_{BB,i}^0 \) there be interatomic distances of atoms in pure metals, and \( r_{AA,i}^1 \) and \( r_{BB,i}^1 \) – in the alloy. Then you can get:

\[ r_{AA,i}^1 = r_{AA,i}^0 + r_{BB,i}^0 - r_{AA,i}^0 C_B, \]

\[ r_{BB,i}^1 = r_{BB,i}^0 - r_{BB,i}^0 C_A. \]

In equations (14) and (15), \( K \) is a fitting parameter. In the proposed model, the displacement parameters will be:

![Fig. 1. Model dependences of interatomic distances between atoms of grades A and B on the concentration of the alloy in a linear approximation. Line 1 is the dependence \( r_{BB,i}^1 \) on concentration, line 3 is the dependence \( r_{AA,i}^1 \) on concentration, and line 2 is the dependence of the radius of the ith coordination sphere \( r_i \) on the alloy concentration. Dotted lines are the distances between atoms in pure metals.](image-url)
\[ \Delta_{AA,j} = \frac{r_{AA,i}^{j}}{r_{i}} - 1 \text{ and } \Delta_{BB,j} = \frac{r_{BB,i}^{j}}{r_{i}} - 1. \] (16)

In (16), \( r_{i} \) is the radius of the \( i \)-th coordination sphere can be estimated by a linear dependence on concentration (in Fig. 1, it is also shown by a solid line).

In this work, the fitting parameter \( K \) was found by fitting the short-range order parameters \( \alpha_{lnm}^{exp} \) of the polycrystalline alloy Ni-14at.%Pt, which was determined from the intensity of diffuse x-ray scattering measured in [1]. Moreover, for a number of \( K \) values, the sums of standard deviations

\[ \sum_{i=1}^{N} \left( \alpha_{i}^{th} - \alpha_{i}^{exp} C_{i} \right)^{2} \]

were calculated where \( C_{i} \) are coordination numbers, and the true value was taken to be the corresponding minimum value. The theoretical values of the Ni-14at.%Pt alloy parameters \( \alpha_{i}^{th} \) were determined by the Krivoglaz–Klepp–Moss method [8] from the ordering energies

\[ V^{th}(r_{i}) \]

calculated by the pseudopotential method. First, the Fourier components of the values \( V^{th}(r_{i}) \) were calculated using the relation

\[ \alpha(\mathbf{k}) = \frac{1}{1 + 2C_{A}C_{B}V^{th}(\mathbf{k})/k_{B}} \]

the Fourier transforms of the short-range order parameters \( \alpha(\mathbf{k}) \) were found. From these values, the short-range order parameters \( \alpha^{th}(r_{i}) \) were determined using the inverse Fourier transform.

To verify the proposed scheme for calculating the ordering energies, we estimated the value of the temperature of the order-disorder phase transition \( T_{\beta}^{th} \), which, according to [9], is related to the value of the Fourier transform of the ordering energy

\[ V^{th}(\mathbf{k}_{m}) = \sum \hat{V}(\hat{r}) e^{i \mathbf{k}_{m} \cdot \hat{r}} \]

by the relation:

\[ T_{\beta}^{th} = \min \left( -\frac{2C_{A}C_{B}V^{th}(\mathbf{k}_{m})}{k_{B}} \right), \] (18)

where \( \mathbf{k}_{m} \) is one of the vectors of the star associated with the order-disorder phase transformation. The calculation was carried out for the reflex (100).

4. CALCULATION RESULTS AND DISCUSSION

During the formation of a solid solution, the sizes of the atoms of the components change [7]. So atoms that were larger in the initial state than in solid solution should decrease in size and fit into the middle lattice of a virtual crystal. In contrast, smaller atoms should increase them. In both cases, the component atoms will be displaced from the nodes of the crystal lattice of the middle crystal, the lattice parameters of which are found from reflections. At the same time, it is important to develop methods for assessing such changes. In this paper, an attempt is made to make such estimates in the simplified model shown in Fig. 1. Table 2 shows the atomic sizes of Ni and Pt in pure metals and in a solid solution of Ni-14at.% Pt. It is seen that in the solid solution, nickel atoms increase their size by 0.033Å to a value of 2.528Å, and platinum atoms decrease by 0.197Å to a value of 2.771Å. In this case, the decrease in the size of platinum atoms exceeds the increase in the size of nickel atoms by almost six times. It turned out that if in the initial state the sizes of nickel and platinum atoms differed by 0.283Å, then this difference in the solid solution was 0.046Å. This largely determined the calculated values of the parameters \( \Delta_{NiNi,i}^{th} \) and \( \Delta_{PtPt,i}^{th} \), which turned out to be equal to -0.0028 and 0.0182, respectively. This ratio corresponds to the predominant contribution of static distortions due to the influence of platinum atoms.

Table 3 shows the values of the ordering energy components \( A(r) \) and \( B(r) \) for the first twelve

| Content, at%Pt | \( r_{i} \) Å | \( r_{m} \) Å |
|---------------|---------------|---------------|
| 0             | 2.488         | 2.488         |
| 14            | 2.528         | 2.521         |
| 100           | 2.771         | -             | 2.771         |
coordination spheres, calculated using the model of the transitional metal potential of Animalu and taking into account static displacements. It can be seen that, in the first sphere, the energy contribution $B(r)$ is twice as large as the component $A(r)$, which indicates the importance of taking into account static displacements in estimating the ordering energy of disordered solid solutions. Also from the data Table 3 shows that, in all other coordination spheres, the contribution of energy $B(r)$ is predominant. This explains the previously failed attempts of such calculations [4-5].

The results of calculating the ordering energies of the Ni-14at.%Pt alloy for the first twelve coordination spheres are shown in the second column of Table 4. They were obtained with a fitting parameter $K$ of 1.233. It is seen that the calculated energies $V^{th}(r)$ corresponding to the minimum of standard deviations $\frac{1}{N} \sum_{i=1}^{N} (\alpha^{th}_i - \alpha^{exp}_i)^2$, with increasing coordination sphere number are of a characteristic alternating character. Comparing the calculated and experimental values of the short-range order parameters of the Ni-14at.%Pt alloy given in the third and fourth columns of the Table, we can note their satisfactory agreement. So for most coordination areas they coincided in sign and were close in magnitude. The value $V(\tilde{k}_m)$ calculated using the obtained ordering energies $V^{th}(r)$ was $-287$ meV, and the value of the order – disorder phase transition temperature was $519^\circ$C, which is consistent with the data given in [10].

In Figure 2 shows the dependence of the ordering energies on the first twelve coordination spheres of the Ni-14at.%Pt alloy on the radius of the coordination sphere. For comparison, in Fig. 2 also shows the dependence of the ordering energies of the single-crystal alloy Ni-23.2at.%Pt in the first eight spheres, calculated in

![Fig. 2. The dependences of the ordering energies for the Ni-14at.%Pt and Ni-23.2 at.% Pt alloys on the radii of the coordination spheres: ○ – for the Ni-14at.%Pt alloy; ■ – for the Ni-23.2 at.% Pt alloy according to [2].]
[2] by the Krivoglaz–Klep–Moss method using short-range order parameters in the first fifteen coordination spheres, which were experimentally determined by the X-ray method. It can be seen from the figure that both dependences have a similar quasi-oscillating character. The values of the ordering energies for the first four and eighth coordination spheres coincided in sign. For the Ni-23.2at.%Pt alloy, the ordering energies in the first two coordination spheres were slightly higher in absolute value than the corresponding values for the Ni-14at.%Pt alloy. In the third and fourth spheres, they turned out to be close in magnitude. In general, their satisfactory coincidence can be noted. This suggests the promise of using pseudopotentials of transition metals [6] for calculating the ordering energies and related characteristics of disordered solid solutions.

5. CONCLUSION
Thus, taking into account the linear size effect in the electronic theory, for the Ni-14at.%Pt alloy, it was possible to carry out a numerical calculation of the ordering energies and the neighbor parameters for twelve coordination spheres. In the calculations, the fitting of the theoretical values of the short-range order parameters to their experimental values determined by the method of diffuse x-ray scattering was used. The contribution of static atomic displacements to the ordering energy is estimated. The obtained values of the ordering energies made it possible to estimate the temperature of the order-disorder phase transition for the Ni-14at.%Pt alloy.

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