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Pseudopotential calculation of thermodynamic properties and glass transition temperatures of binary Ni–Al alloys

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Abstract. The pseudopotential method and thermodynamic perturbation theory are applied to investigate the thermodynamics of Ni–Al alloys. The Einstein model approximation in the solid phase and the Percus–Yevick hard-sphere approximation in the liquid phase are chosen as reference systems. In all the calculations the local Animalu pseudopotential and the non-local pseudopotential with resonant contribution in the case of a transition metal are used. The static concentration-wave method is applied to investigate the ordering process in the solid phase. Taking charge transfer into consideration within the framework of the non-local resonant potential model, we have described the features of the main excess mixing characteristics and the dynamic viscosity in the liquid system studied. It is shown that in Ni₅₀Al₅₀ alloy the Kauzmann reduced temperature is higher than in pure Ni but insufficient for ready glass formation.

1. Introduction

In accordance with the Miedema classification [1], two requirements must be met for ready glass formation (RGF) to occur: $\Delta H < -5 \text{ kcal mol}^{-1}$ and $r_1/r_2 \leq 0.85$ (ΔH is the heat of mixing, r_1/r_2 is the atomic ratio). In conformity with this criterion the Ni–Al system is more preferable among 3d transition metal–Al alloys: this system is non-RGF but in the H – R map it is found near the line that divides RGF and non-RGF regions [2–5].

The strong interaction between unlike components is the distinctive feature of RGF systems characterized by the considerable compression and the large negative heat of mixing. In recent work [6, 7] within the framework of the local Animalu model pseudopotential (MP) we have calculated the main thermodynamic properties of liquid Ni–Al alloys. We could not describe the observed large negative deviation from ideality [8, 9] and the viscosity peak near the equiatomic composition [10] in the system under consideration. The Animalu MP does not enable one to take into account the change of electronic structure when the transition metal is alloyed with a polyvalent one. In accordance with the existing viewpoint the strong interaction between unlike atoms in such systems as the transition metal–polyvalent metal is interpreted from the filling of

the d band of the transition metal as it is alloyed with a polyvalent one. In the present work we have set the task to describe this phenomenon within the framework of the non-local MP in the case of a simple metal [11, 12] and its resonant modification in the case of a transition metal [13].

The general scope of this paper is as follows. In section 2 a general expression for the Helmholtz free energy of the binary alloy based on the use of pseudopotentials and the Gibbs–Bogoliubov inequality is presented. In section 3 we construct the non-local MP in the case of a simple metal and its resonant modification in the case of a transition metal. The calculated melting characteristics of Ni are presented in section 4. We have also calculated the Kauzmann temperature for liquid Ni. Section 5 is dedicated to the calculation of the equilibrium volume, and the energy and entropy of mixing of liquid Ni–Al alloys. We quote our results of the dynamic viscosity calculation and analyse its peculiarities. In section 6 the calculation of the Kauzmann temperature for Ni₅₀Al₅₀ alloy is presented. In the case of the solid phase the thermodynamic statistical theory of ordering is used in order to calculate the Helmholtz free energy. The temperature dependence of the ordering potential is investigated.

2. The construction of the Helmholtz free energy

The Helmholtz free energy (F) is calculated in second-order perturbation theory with the pseudopotential formalism, and thermodynamic perturbation theory is also used [14, 15]. To describe the reference systems the Einstein model in the solid phase and the Percus–Yevick (PY) hard-sphere (HS) approximation in the liquid phase [16] are used. The Carnahan–Starling expression was chosen to calculate the entropy of melting [17]. The Geldart–Vosko [18] and Shaw [19] screening functions were applied in the calculations of the characteristic function in the case of the local and non-local MP respectively. According to the Gibbs–Bogoliubov inequality the following expression is valid:

$$F \leq \langle K \rangle_0 + E_0 + E_1 + \langle E_2 \rangle_0 + \langle E_3 \rangle_0 - TS_0. \quad (2.1)$$

Here K is the kinetic energy of ions, E_0 is the sum of kinetic, exchange and correlation energies of a uniform electron gas, E_1 is the Hartree energy, $\langle E_2 \rangle_0$ is the band-structure energy, $\langle E_3 \rangle_0$ is the Ewald energy, and $\langle \dots \rangle_0$ represents averaging over the reference system. S_0 is the entropy of the reference system. For the solid phase

$$S_0 = S_\theta + S_{\text{conf}} + S_{\text{eg}} \quad (2.2)$$

where S_{conf} is the configuration entropy calculated in the ideal mixture approximation, S_θ is the vibrational entropy in the Einstein approximation and S_{eg} is the electron-gas entropy.

For the binary system of hard spheres

$$S_\sigma = S_{\text{gas}} + S(\eta) + S_{\text{conf}} + S(\Delta\sigma) + S_{\text{eg}} \quad (2.3)$$

where S_{gas} is the perfect-gas entropy, $S(\eta)$ is the packing entropy and $S(\Delta\sigma)$ is an addend, which is solely due to the presence of spheres with different diameters in the mixture. In all the following calculations we use the atomic units system (au) where $\hbar = m_e = |e| = 1$.

The values of the equilibrium atomic volume (Ω_0) were determined from the pressure equation of state and the optimum parameters of reference systems were found by minimizing the right-hand side of inequality (2.1).

Detailed expressions of the Helmholtz free-energy contributions are published in [20]. We have used the well known non-local formalism [19, 21–24] to calculate the Ewald energy and the pseudopotential characteristic functions.

3. The construction of the non-local model pseudopotential

3.1. Simple metal

In order to reproduce the MP's disperse ability similar to a real one we must describe free-ion term values. This is the main principle on which the Heine–Abarenkov (HA) approach is based. In accordance with the HA original form the ion core was interpreted as a 'black box'. In other words the HA MP shape was not defined uniquely inside the ion core. Different potentials with different behaviours in the ion core region which are able to reproduce free-ion term values can lead to still different results in the calculations of both electronic and atomic properties of metals. In order to avoid this ambiguous behaviour in the ion core region it is necessary to input an additional parameter to change the potential form using the well based *a priori* criterion—the thermodynamic equilibrium condition.

In accordance with the Vatin–Yuryev–Gelchinskii scheme [11, 12] one can write the free-ion MP in direct space as follows:

$$\omega_0(r, E) = -\frac{Z_2}{r} + \sum_{l=0}^{l_0} \theta(R_M - r) \left(A_l(r, E) + \frac{Z_2}{r} \right) Q_l \quad (3.1)$$

where Z_2 is the simple metal valence, l is the angular momentum index, θ is the Heaviside function, and Q_l is the projection operator which picks out the l th angular momentum part. R_M is chosen as half of the sum of the atomic and ionic radii.

In reciprocal space the non-screened form of the non-local MP is written as follows:

$$\omega_0(k, q) = V_q + f(k, q) \quad (3.2)$$

where $V_q = -4\pi Z_2 / \Omega q^2$ is the Fourier transform of the Coulomb potential and

$$f(k, q) = \frac{4\pi}{\Omega} \sum_{l=0}^{l_0} (2l+1) P_l(\cos \theta) \times \int_0^{R_M} dr r^2 \left(A_l(r, E) + \frac{Z_2}{r} \right) j_l(kr) j_l(|k+q|r) \quad (3.3)$$

is connected with non-local MP part. Here $P_l(x)$ is a Legendre polynomial, $j_l(x)$ is a spherical Bessel function, and θ is the angle between k and $k+q$.

The non-local MP under consideration shows coulombic behaviour outside the core and is described by a polynomial of degree 3 in the ion core region:

$$A_l(r, E) = -\frac{Z_2}{R_M} \left[a_l + b_l \left(\frac{r}{R_M} \right) + c_l \left(\frac{r}{R_M} \right)^2 + d_l \left(\frac{r}{R_M} \right)^3 \right]. \quad (3.4)$$

Under smooth conditions on the core sphere (R_M) one can exclude two parameters:

$$b_l = -2a_l + d_l + 3 \quad c_l = a_l - 2d_l - 2. \quad (3.5)$$

Thus we have two independent parameters for each l component of the constructed

MP: a_l and d_l . The parameter a_l allows one to change the pseudopotential form by the definition of the $\omega'_0(r = 0)$ value (ω'_0 corresponds to the l th angular momentum part), and d_l is chosen from the following condition [12]: $\omega_0(r)$ must satisfy the Schrödinger equation with the self-energy E_l taken from ionic term values [25]. This scheme enables one to find the parameter d_l by arbitrary fixed values of the parameter a_l . For an equivalent form of the MP one can use the thermodynamic equilibrium condition at the melting point (Al: $T_m = 933$ K) together with the description of the free-ion term values. Besides it is necessary to use a very strong condition—the melting temperature description ($F_s(T_m) = F_l(T_m)$). In the case of a simple metal (Al): $Z_2 = 3$, $R_M = 1.9$, $a_0 = 8.019$, $a_1 = -8.0$, $d_0(E'_F) = -21.490$, $d_1(E'_F) = 12.097$, $\partial d_0/\partial E' = -3.7523$, $\partial d_1/\partial E' = 0.7495$ (au), where E'_F is Fermi energy with respect to the free ionic energy E_m [26]. In the pioneer works [11, 12] the parameters were obtained from the equilibrium condition at $T = 0$ K.

3.2. Transition metal

In the case of a transition metal we can observe the d resonant effect when the energy of s-p electrons is equal to the centre of gravity of the d band. The non-local resonant MP is built up as a sum of the non-resonant contribution $\omega_0(r)$, which is responsible for the weak s-p dispersion, and the resonant one $V_{res}(r, E)$, which influences only the d part of the wavefunction [27, 28]. In reciprocal space

$$V_0(k, q) = \omega_0(k_F, q) + V_{res}(k, q) \tag{3.6}$$

where $\omega_0(k_F, q)$ coincides with (3.2) in the Fermi sphere approximation and $V_{res}(k, q)$ reflects the s-d hybridization and influences only the d part of the wavefunction. In accordance with [23, 28] we can write

$$V_{res}(k, q) = \frac{5}{4\pi} P_2(\cos \theta) \gamma(k) \gamma(|k + q|) \frac{E_k - E_d}{(E_k - E_d)^2 + (0.5W_d)^2} \tag{3.7}$$

Here $\gamma(k)$ is the hybridization matrix element. Taking into consideration [29, 30] that, when $k \rightarrow 0$, $\gamma(k) \sim k^2$ and γ falls to zero outside the first Brillouin zone, one can suppose the following expression:

$$\gamma(k) = \frac{A_d}{\Omega^{1/2}} \left(\frac{k}{k_d}\right)^2 \exp\left(\frac{k_d^2 - k^2}{k_0^2}\right) \tag{3.8}$$

where $k_0 = (6\pi^2/\Omega)^{1/3}$ is the Brillouin zone radius, $k_d = (2E_d)^{1/2}$ characterizes the d-zone position, and $E_k = 0.5k^2$. A_d is the resonant MP amplitude connected with d band width (Δ) [13, 29]:

$$A_d = \Delta(\pi\Omega/5)^{1/2} \tag{3.9}$$

We use the following expression [23] for density of the d states:

$$n_d(E) = \frac{10}{\pi} \frac{0.5W_d}{(E - E_d)^2 + (0.5W_d)^2} \tag{3.10}$$

to obtain the expression (3.7). Here E_d is the centre of gravity of the d band and W_d is the d resonant width. If we integrate (3.10) from $-\infty$ to E_F and equate the result to the

d electron valence Z_d , the Friedel equation for the description of the d band position with respect to the Fermi level will be obtained:

$$E_d = E_F + 0.5W_d/\tan(0.1\pi Z_d). \quad (3.11)$$

In the present work the following parameters of the non-local resonant MP obtained in [13] are used: $Z_1 = 1$, $R_M = 2.2$, $a_0(E_F) = 16.0$, $a_1(E_F) = 35.442$, $a_2(E_F) = 35.442$, $d_0(E_F) = -35.235$, $d_1(E_F) = -52.459$, $d_2(E_F) = -21.433$, $Z_d^0 = 9$, $A_d = 0.938$, $W_d = 0.034$. Here W_d and Δ are quoted from [30] and the expression (3.9) is used to obtain A_d . R_M is chosen as half of the sum of atomic and ionic radii. Parameters a_i and d_i enable one to describe free-ion term values of Cu^+ (see [13]) and the equilibrium density of solid Ni at $T = 0$ K and reflect the equality of Helmholtz free energies of both phases at the melting point (Ni: $T_m = 1726$ K) with high accuracy.

4. The calculation of the melting thermodynamic characteristics and the Kauzmann temperature: application to Ni

At present widespread methods for the rapid solidification of metal alloys enable one to reach cooling rates from 10^4 to 10^7 K s^{-1} [1]. These are not enough to quench an amorphous phase in pure liquid metals. As shown in [31, 32] quenching rates $\sim 10^{12}$ – 10^{13} K s^{-1} are necessary to obtain a single-component metallic glass in Ag, Cu, Ni and Mo. In [33] single-component metallic glasses (Ni and Mo) were obtained. A new method for the explosive spraying of the melt was used. The amorphous Ni crystallization temperature $T_c \approx 570$ K close to the glass transition temperature (T_g) was determined. In [34] the low limit for the glass transition temperature was estimated as the Kauzmann point (Na, Pb and Mg). The investigations mentioned above have stimulated the present calculations, which aimed to model the cooling of liquid Ni up to the glass transition temperature.

Figure 1 shows the interatomic potential $V(r)$ at the melting point in both pseudo-potential approximations mentioned above. The non-local potential is deeper and shifted towards the origin. This behaviour reflects the stronger interaction within the framework of the resonant MP and influences the current results.

Table 1 lists the thermodynamic characteristics of Ni calculated at the melting point. $\Omega_{s(l)}$ is the atomic volume in solid (liquid) Ni, $\Delta\Omega$ and ΔS are the volume and the entropy of fusion, respectively, η is HS packing fraction, and θ_D is the Debye temperature. The stronger interatomic interaction in the non-local approximation enables one to improve the results of the variational parameter calculation in comparison with the Animalu MP. The good agreement between the calculated values and the experiment is a necessary condition for satisfactory calculation of the glass transition temperature.

Figure 2 gives the results of the Kauzmann temperature calculation for Ni. The calculation was performed on the basis of the following criterion [34, 41]: When the temperature approaches T_g a configurational part of the entropy of the liquid vanishes, thus the entropy of the liquid (S_l) decreases faster than that of the solid (S_s). When the melt is frozen below a critical temperature (T_s), $S_l < S_s$ (Kauzmann paradox). T_s is the characteristic temperature of Kauzmann theory and it corresponds to the low limit for T_g in the limit of the low (critical) cooling rate.

According to the present calculations there are $T_s^{(A)} = 1130$ K and $T_s^{(R)} = 800$ K. As mentioned above $T_g^{\text{exp}} \approx 570$ K [33]. The resonant MP enables one to obtain the more realistic value of T_s . As mentioned in [42] the glass transition associated with the

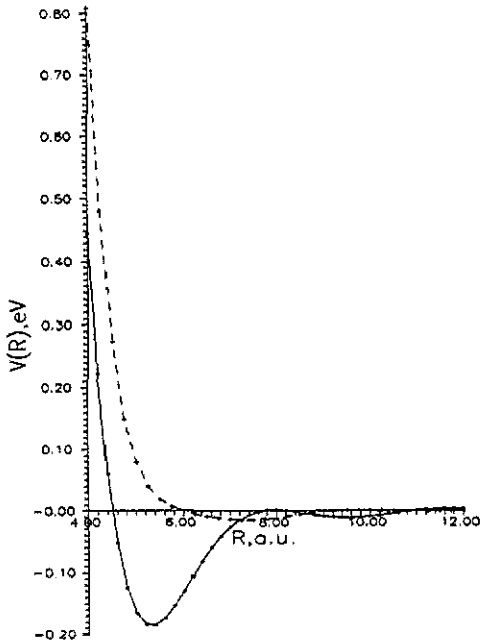


Figure 1. The interatomic potential of liquid Ni: (—) the resonant MP; (----) the Animalu MP.

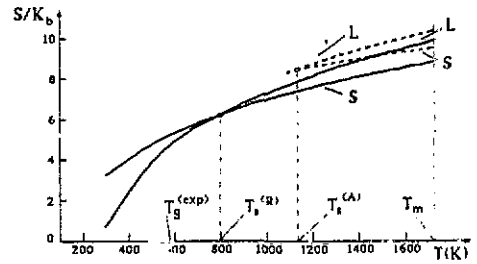


Figure 2. The calculation of Ni Kauzmann temperature: (—) the resonant MP; (----) the Animalu MP.

Table 1. The theoretical and experimental melting characteristics of Ni.

MP	Ω_s (au)	Ω_l (au)	$\Delta\Omega$ (%)	$\Delta S/k_B$	η	θ_D (K)
Animalu	88.62	84.05	-5.16	0.82	0.423	268
Resonant	77.34	82.73	6.97	1.09	0.462	374
Experiment (and reference)	80.64 [35]	83.23 [35] 84.02 [36]	3.21 [35] 4.19 [36]	1.11 [37] 1.23 [38]	0.450 [39]	375 [40]

Kauzmann phenomenon cannot occur for substances of limited molecular weight with physically reasonable potentials. The real glass transition always occurs by $T_g > T_s$.

As mentioned in [34] the correct description of the glass transition temperature of alkali metals based on the Kauzmann criterion ($T_s \approx 0.4T_m$) is possible only within the framework of the Weeks–Chandler–Andersen (WCA) model (liquid state) and the quasi-harmonic phonon model (solid state). Similar calculations performed in [34] within the HA MP and variational PY HS model led to too high results ($T_s \approx 0.57T_m$). Analogously one can explain the too high present result ($T_s \approx 0.66T_m$) obtained in the local Animalu pseudopotential approach. Taking into account the resonant peculiarities of the transition metal within the framework of the non-local MP, one can more reliably describe the interatomic interaction and satisfactorily calculate thermodynamic characteristics. All these provide the lowest T_s ($T_s \approx 0.46T_m$) even within the framework of the simple reference models under consideration.

5. The calculation of the thermodynamic properties of liquid Ni–Al alloys

The non-local pseudopotential method expounded above enables one to describe the bonding energy, bulk moduli and phonon spectra of solid metals and also compressibility, heat capacity, entropy and electrical resistivity of pure metallic melts [11–13]. In the present work we calculate the thermodynamic characteristics of liquid Ni–Al alloys at a fixed temperature and within the whole concentration interval.

The interpretation of the deviation from ideality is the main problem of solution theory. This deviation is characterized by such thermodynamic values as volume (ΔV), energy (ΔE) and excess entropy (ΔS^E) of mixing. All these characteristics are important parameters of many phenomenological models of the glass transition. Many attempts based on different approaches were made in order to describe the deviation from the Zen law:

(i) The association concept with finite lifetime has proved to be very useful in the theory of liquid alloys [43].

(ii) Taking into consideration the electron density rearrangement due to charge transfer in order to cancel the chemical potential difference, the atomic volume change of the alloy can be described [44].

The first approach is realized in many phenomenological models. Taking into consideration the charge transfer within the framework of an *a priori* model we can realize the second approach.

The charge transfer in Mn(Fe,Co,Ni)–Al alloys was investigated in [45] by use of soft x-ray spectroscopy. The experiments have shown that there was a filling of the d band of the transition metal after it was alloyed with the polyvalent metal (Al). Moreover at a critical concentration of Al (c_2^*) the d band was completely filled. Detailed photoemission studies have already ascertained [46] that the density of states near the Fermi level ($n_d(E_F)$) in the equiatomic Ni–Al alloy is much lower than in pure Ni. Usually this critical concentration is found by diamagnetic transfer conditions when the d band is completely filled [46, 47]. In [48] the theoretical method of the definition of c_2^* was elaborated. In the present calculation we have used $c_2^* = 0.55$ [47].

In accordance with the existing d band filling mechanism [46–49] there are two sets of equations to calculate Z_s and Z_d :

(i) $0 \leq c_2 \leq c_2^*$ (d band is unfilled)

$$Z_d = Z_d^0 + (10 - Z_d^0)c_2/c_2^* \quad (5.1)$$

$$Z_s = Z_1c_1 + (Z_2 - n_c)c_2. \quad (5.2)$$

Here n_c is the number of valence electrons transferred into the d band; n_c is found from the balance condition at $c_2 = c_2^*$:

$$n_c c_2^* = (10 - Z_d^0)(1 - c_2^*). \quad (5.3)$$

In the present calculations $n_c = 0.8132$. Taking into consideration $W_d = 0$ when the d band is completely filled [13] we have assumed a linear d resonant width decrease to zero within the same concentration range:

$$W_d = W_d^0(1 - c_2/c_2^*) \quad (5.4)$$

where W_d^0 is the d resonant width of pure Ni.

(ii) $c_2 \geq c_2^*$ (d band is filled)

$$Z_d = 10 \quad Z_s = (Z_1 + Z_d^0 - 10)c_1 + Z_2c_2 \quad (5.5)$$

$$W_d = 0 \quad n_d(E_F) = 0 \quad (5.6)$$

$$E_d = E_F + \lim_{c_2 \rightarrow c_2^*} [0.5W_d/\tan(0.1\pi Z_d)]. \quad (5.7)$$

We have taken into account that the second term in (5.7) transforms to 0/0 type when the d band is filled. The concentration point c_2^* belongs to both intervals mentioned above. That is why we have used the limit transition in (5.7).

In [20] to save computing time we have considered non-local effects only for Ni (in Al non-local effects are very small). Thus in this model the Ni depletion hole charge changed but the Al one became constant within the whole concentration interval. In order to avoid this discrepancy we have selected the resonant MP amplitude to describe the experimental value of the heat of mixing in the given system.

In contrast to [20] the present calculations were performed within the framework of the whole non-local model without the use of any thermodynamic experimental information on Ni–Al alloys. We have used the depletion hole charge balance equation:

$$c_1(\rho_{Ni} - \rho_{Ni}^0) + c_2(\rho_{Al} - \rho_{Al}^0) = 0 \quad (5.8)$$

where $\rho_{Ni(Al)}$ is the depletion hole charge for Ni (Al) in the alloy and $\rho_{Ni(Al)}^0$ is the same value in the pure metal. We have solved this equation with respect to the resonant MP amplitude.

Calculated values of the s–p electron density (Z_s/Ω), depletion hole charges and the resonant MP amplitude are plotted in figure 3. With Al concentration increasing, the electron density increases too. It leads to the Ni depletion hole increasing in order to compensate the electron density growth. When Ni atoms are dissolved in Al, the Al depletion hole decreases.

The calculated values of the equilibrium volume, and the energy and excess entropy of mixing are plotted in figure 4 ($T = 1923$ K). Experimental results were taken from [8, 9, 50]. The present calculations show a small deviation from the Zen law when $c_2 \leq 40$ at. % and a large negative deviation within the rest of the concentration interval. The calculated mixing energy is several times as high (when Al is dominant in Ni–Al alloys) as the experimental one. The calculations performed in [6] (Animalu MP) do not enable one to describe the considerable negative excess entropy of liquid Ni–Al alloys. The excess mixing entropy calculated in the non-local approach is in good agreement with the experimental data under consideration; moreover $\Delta S_E \ll 0$ when $c_2 > 40$ at. %. There are two reasons for this behaviour: first, the large volume compression, which leads to the negative packing entropy contribution to ΔS^E ; secondly, d band filling leads to the negative electron entropy contribution to ΔS^E [48]. As mentioned in [41] the glass transition temperature attains a maximum at the same concentration point where ΔS^E reaches a minimum. One can explain this coincidence on the basis of the Kauzmann criterion [34, 41]. But the reduction of the entropy of liquid alloys, unlike a pure metal, is due not only to the cooling but to the volume compression too.

Calculated values of HS diameters and HS packing fraction are plotted in figure 5. Figure 6 shows the dynamic viscosity concentration dependence at $T = 1923$ K. The experimental viscosity results were published in [10]. Taking into consideration the change in depletion hole charge mentioned above one can explain the observed HS diameter behaviour. Both the considerable Ni HS change within the concentration range

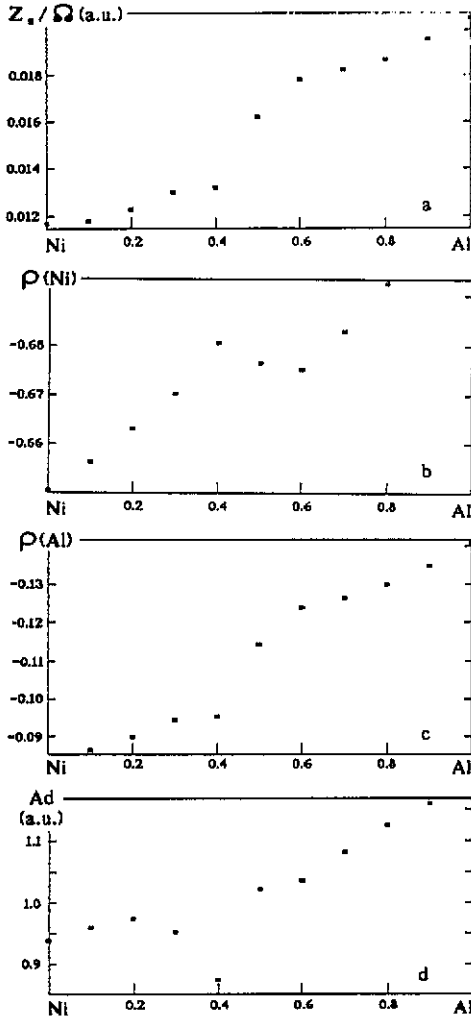


Figure 3. The concentration dependence of: (a) the s - p electron density; (b) the Ni depletion hole charge; (c) the Al depletion hole charge; (d) the resonant MP amplitude.

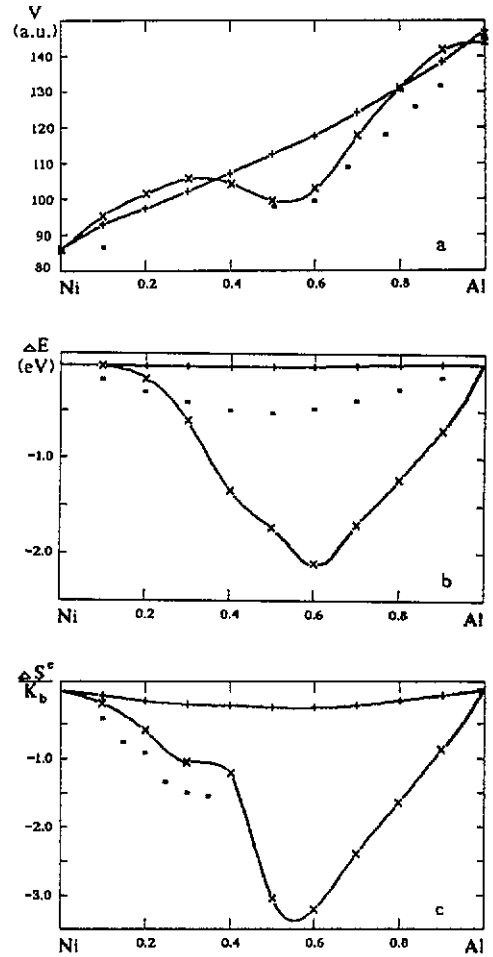


Figure 4. The concentration dependence of: (a) the equilibrium volume; (b) the energy of mixing; (c) the excess entropy of mixing. $T = 1923$ K. Symbols: (x) the resonant MP; (+) the Animalu MP; (■) experiment [8, 9, 50].

and the volume compression lead to a large positive HS packing fraction deviation from additivity. It shows up in the viscosity of liquid Ni-Al alloys, which was calculated within the framework of the Enskog model (the working formulae are given in [7]). We are able to describe the viscosity peak within the framework of the non-local MP although it becomes wider and probably too high compared with the experimental one. Nevertheless, we can take into account the principal possibility of such peak description within the framework of the atomic viscosity model without using the association mechanism. Taking into consideration viscosity and entropy extremum position near the equiatomic composition, we have chosen $\text{Ni}_{50}\text{Al}_{50}$ alloy to calculate the Kauzmann temperature.

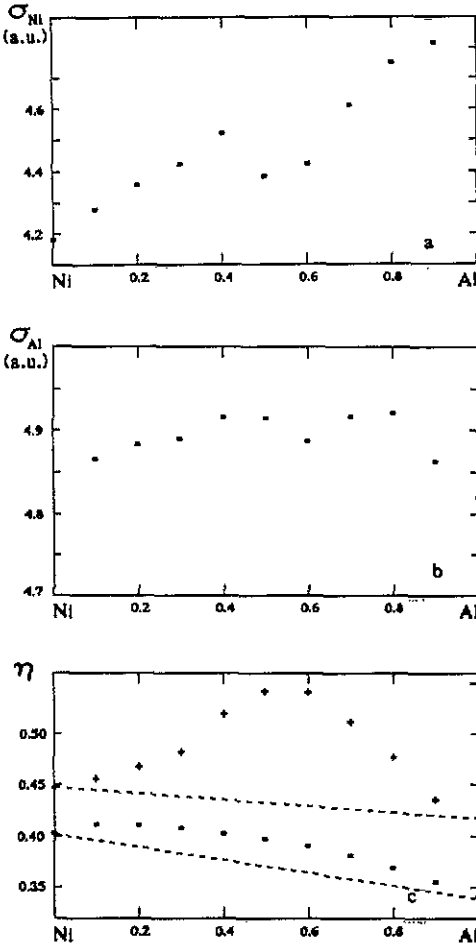


Figure 5. The concentration dependence of (a) the Ni HS diameter; (b) the Al HS diameter (the resonant MP); (c) the HS packing fraction. Symbols in (c): (+) the resonant MP; (■) the Animalu MP.

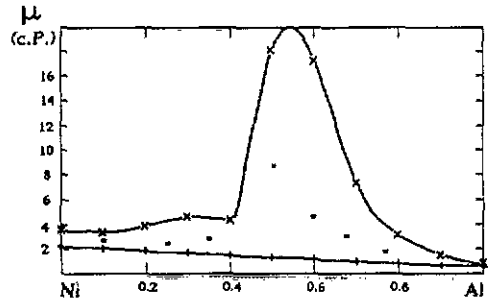


Figure 6. The dynamic viscosity concentration dependence of liquid Ni-Al alloys. $T = 1923$ K. Symbols: (x) the resonant MP; (+) the Animalu MP; (■) experiment [10].

6. The calculation of the Kauzmann temperature in $Ni_{50}Al_{50}$ alloy

As shown in section 2, the Helmholtz free energy of the disordered binary solid solution can be calculated by means of inequality (2.1) with the Einstein oscillator system as the reference state. Ordering results in an additional contribution to the energy expression (ordering energy) and to the account of the long-range order parameter in the entropy term. In [51] the pseudopotential method and thermodynamic perturbation theory were used to investigate the ordering of Mg_3Cd and $MgCd_3$ phases; moreover the long-range parameter (τ) was determined by means of the variational approach. This approach has an essential deficiency: experimental information on the type of superstructure under investigation must be known. In [41] the Kauzmann criterion was used to investigate the liquid-glass transition in $Ca-Mg$ and $Mg-Zn$ systems and the ordering entropy

information was taken from experiment. At the same time it is interesting to make an *a priori* determination of the energetically favourable superstructure arisen on the basis of the given lattice of the disordered solid solution. The solution of this problem becomes possible due to the joint employment of both the pseudopotential method and the thermodynamic statistical theory of ordering [52–54]. This approach was used in [55–57] to investigate the ordering effects in the Ni–Al system (Animalu local MP). It was found that the superstructures B2 (NiAl) and L1₂ (Ni₃Al) based on BCC and FCC lattice, respectively, were the most favourable (our present non-local calculations give the same result) and the phase diagram in the two-phase region between NiAl and Ni₃Al was plotted.

In order to calculate the ordering contribution to the Helmholtz free energy of the binary solution it is necessary to know the Fourier transform of the ordering potential $V(k_s)$. Here k_s is one of the wavevectors of the star which characterizes the stability of the given superstructure. For the superstructure B2 under consideration, $k_s = (111)$. As shown in [52–54]

$$V(k_s) = 2 \sum_{q_0} \tilde{F}_{\text{sub}}(q_0 + k_s) - \frac{2\Omega}{(2\pi)^3} \int dq \tilde{F}_{\text{sub}}(q) \quad (6.1)$$

where

$$\tilde{F}_{\text{sub}}(q) = F_{\text{sub}}(q) + (2\pi/\Omega q^2)(Z_1^* - Z_2^*)^2 \exp(-q^2/4\nu). \quad (6.2)$$

Here $F_{\text{sub}}(q)$ is the subtractive pseudopotential characteristic function, $Z_{i(2)}^*$ is the effective ion valence and ν is the Ewald parameter (see appendix).

Knowing the ordering potential $V(111)$ one can calculate the long-range order parameter for B2 superstructure by means of the equation [52]:

$$\ln \frac{(c_1 - 0.5\tau)(c_2 - 0.5\tau)}{(c_1 + 0.5\tau)(c_2 + 0.5\tau)} = \frac{V(111)\tau}{k_B T}. \quad (6.3)$$

The ordering energy for B2 phase can be written as follows [52]:

$$\Delta U_{\text{ord}} = \frac{1}{3}V(111)\tau^2 \quad (6.4)$$

and the configuration entropy must be written as follows [58]:

$$S_{\text{conf}}^{\text{ord}} = -\frac{1}{2}k_B [(c_1 + 0.5\tau) \ln(c_1 + 0.5\tau) + (c_1 - 0.5\tau) \ln(c_1 - 0.5) + (c_2 + 0.5\tau) \ln(c_2 + 0.5\tau) + (c_2 - 0.5\tau) \ln(c_2 - 0.5\tau)]. \quad (6.5)$$

In the present calculation of the Helmholtz free energy of the ordered solid solution we have the following scheme: In order to obtain $\rho_{\text{Ni(Al)}}$ we have solved the pressure equation of state for pure components and thus using (5.8) and the common variational scheme the equilibrium volume of the disordered solid solution was found. This volume was used to calculate $F_{\text{sub}}(q)$ and r_0 , $Z_{i(2)}^*$ —to define Ewald parameter ν (see appendix). Then using (6.1)–(6.5) one can calculate $V(111)$, τ , ΔU and $S_{\text{conf}}^{\text{ord}}$.

In accordance with [57] within the framework of Animalu MP for B2 phase of Ni₅₀Al₅₀ alloy the following result is obtained: $V(111) = -0.0737$ at $T = 0$ K, which corresponds to the order–disorder transition temperature $T_c^0 = 5818$ K calculated by the formula [52]:

$$T_c^0 = -c_1 c_2 V(111)/k_B. \quad (6.6)$$

The above index '0' means that the ordering potential is calculated at $T = 0$ K and is

Table 2. The ordering potential $V(111)$ (in au) temperature dependence in $\text{Ni}_{50}\text{Al}_{50}$ alloy.

T (K)	2300	1900	1500	1100
$V(111)$	-0.0535	-0.0597	-0.0657	-0.0706

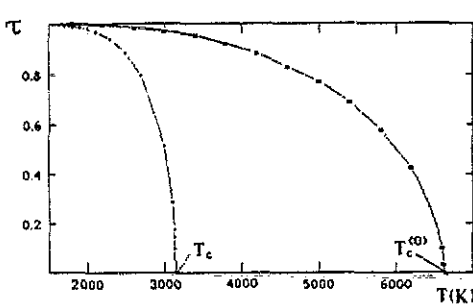


Figure 7. The temperature dependence of the long-range order parameter in B2 phase $\text{Ni}_{50}\text{Al}_{50}$ (the resonant MP). Symbols: (■) without account of $V(111)$ temperature dependence; (+) with account of $V(111)$ temperature dependence.

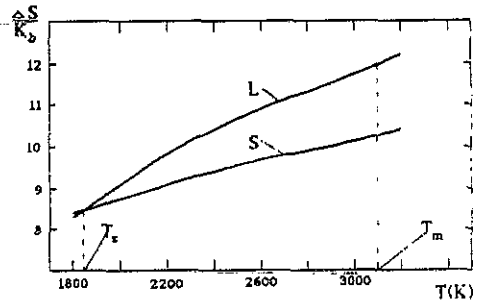


Figure 8. The calculation of $\text{Ni}_{50}\text{Al}_{50}$ Kauzmann temperature (the resonant MP).

temperature-independent. The present calculations with the non-local MP give the following results: at $T = 0$ K and $V(111) = -0.0839$, $\tau = 1$ and $T_c^0 = 6642$ K. But the approach under consideration allows one to show the reduction of the ordering potential with increasing temperature. This temperature dependence is reflected in table 2. Using equation (6.3) one can construct the temperature dependence of the long-range order parameter $\tau(T)$ with the account of the temperature dependence of $V(111)$. The calculations are performed up to the order-disorder temperature (T_c) and the results are plotted in figure 7. The results of the calculation with the non-local MP and without taking account of the $V(111)$ temperature dependence are plotted too. The calculated critical temperature is $T_c = 3140$ K, and is considerably smaller than T_c^0 quoted above.

Figure 8 gives the result of the Kauzmann temperature calculation for $\text{Ni}_{50}\text{Al}_{50}$ alloy performed within the framework of the non-local MP. According to the calculations $T_s^{(th)} \approx 1830$ K and $T_m^{(th)} \approx 3100$ K. $T_s = 0.59T_m$ is higher than the same value of pure Ni ($T_s = 0.46T_m$) but too low for RGF.

7. Conclusions

The use of two different quantum-mechanical models of the interatomic interaction (the pseudopotential method and the tight-binding approximation) and the thermodynamic variational methods is standard in work devoted to research on the thermodynamic characteristics of binary metallic alloys. Most of them are dedicated to simple metal alloys where the use of the local MP is correct [14, 15, 51, 59]. However, in systems with a significant deviation from ideality, good agreement with experiment can be reached only by the use of the non-local pseudopotential. For an example one can look through

the works [41, 60] where the first-principles orthogonalized plane-wave (OPW) pseudopotential was used. In [61] chemical short-range order (CSRO) investigations in the liquid and amorphous alloys of simple metals based on the OPW method and Yukawa charge hard-sphere (YHS) reference system were made. Use of both the tight-binding model and the Yukawa formalism was made in the works [62, 63] to investigate CSRO in liquid and amorphous transition metal-transition metal (T-T) alloys.

The present work is devoted to the transition metal-polyvalent metal (T-P) Ni-Al system. The use of the local MP [6, 7] does not allow one to show the main distinguishing feature of this system—the large negative deviation from ideality. This problem can be solved only in terms of the complete non-local approach with resonant mechanism interaction. The correct account of the electron effects when a transition metal is alloyed with a polyvalent metal allows one to describe the peculiarities of the main thermodynamic and kinetic characteristics of T-P liquid alloys which are necessary to estimate the glass transition ability. It is very important to take into consideration both d band filling and depletion hole change around each component. One can describe rather well the strong negative deviation from ideality without use of the association mechanism.

The Kauzmann temperature calculations for Ni and Ni₅₀Al₅₀ were performed. It is shown that in the alloy under consideration the Kauzmann reduced temperature (T_s/T_m) is higher than that in pure Ni but insufficient for RGF.

Acknowledgment

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Appendix

As was shown in [52] the electrostatic contribution to the ordered energy of a completely ordered alloy with two types of sites in pseudopotential theory can be represented as:

$$\Delta E_{\text{es}} = \frac{1}{2}(Z_1^* - Z_2^*)^2 \left[\frac{4\pi}{\Omega} \sum_{q_0} \frac{1}{|g_0 + k_s|^2} \exp\left(-\frac{|q_0 + k_s|^2}{4\nu}\right) - 2\left(\frac{\nu}{\pi}\right)^{1/2} \right] c_1 c_2. \quad (\text{A1})$$

In accordance with [52–54] the Ewald parameter ν in (A1) is chosen so that the contribution from direct space may be ignored.

On the other hand ΔE_s is the difference between the electrostatic energies of completely ordered and completely disordered alloys. Therefore from the condition of the limit transition from the completely ordered state to the completely disordered one, within the framework of the statistical concentration-wave model [52] the electrostatic contribution in the Fourier transform of the mixing potential $V_{\text{es}}(\mathbf{k}_s)$ can be written as:

$$V_{\text{es}}(\mathbf{k}_s) = (2/c_1 c_2) \Delta E_{\text{es}}. \quad (\text{A2})$$

But Ewald's sum in (A1) depends only upon both the basic crystal and the ordered substructures. Therefore $V_{\text{es}}(\mathbf{k}_s)$ may be expressed as

$$V_{\text{es}}(\mathbf{k}_s) = \alpha_M^{\ddagger} (Z_1^* - Z_2^*)^2 / r_0 \quad (\text{A3})$$

where α_M^{\ddagger} is the Madelung constant for the given superstructure.

Let us show that in the case when all sublattices of the ordered alloy are crystallographically equivalent (for instance, two sublattices in superstructure B2) α_M^s may be expressed over Madelung constants of the basic lattice.

Let the basic lattice contain n crystallographically equivalent sublattices, and in the completely ordered state k of them are occupied by atoms of type A and m by atoms of type B. From the equivalence of these sublattices one can obtain the following relation between Madelung constants [64]:

$$\alpha_{ii} = \alpha_{jj} \equiv \alpha_{11} \quad \text{and} \quad \alpha_{ij} = \alpha_{pq} \equiv \alpha_{12} \quad (i \neq j; p \neq q). \quad (\text{A4})$$

In this case the electrostatic energy of the completely ordered alloy will be expressed in the following way:

$$E_{cs} = [1/(2nr_0)][k\alpha_{11}(Z_1^*)^2 + m\alpha_{11}(Z_2^*)^2 + k(k-1)\alpha_{12}(Z_1^*)^2 + m(m-1)\alpha_{12}(Z_2^*)^2 + 2\alpha_{12}mkZ_1^*Z_2^*]. \quad (\text{A5})$$

After some easy algebra

$$E_{cs} = [1/(2r_0)][\alpha_0(c_1Z_1^* + c_2Z_2^*)^2 + (mk/n^2)(\alpha_{11} - \alpha_{12})(Z_1^* - Z_2^*)^2]. \quad (\text{A6})$$

Here α_0 is a 'full' Madelung constant of the basic lattice:

$$\alpha_0 = \alpha_{11} + (n-1)\alpha_{12}. \quad (\text{A7})$$

It is obvious that the first term in (A6) is equal to the energy of completely disordered solid solution [52] and hence the second term must be equal to ΔE_{cs} (A1). Owing to this discussion one can immediately obtain

$$\alpha_M^s = (\alpha_{11} - \alpha_{12}). \quad (\text{A8})$$

For the B2 structure $\alpha_{11} = -1.397007$, $\alpha_{12} = -0.394851$ ($\alpha_0^{B2} = \alpha_M^{BCC} = -1.7918585$); for the $L1_2$ structure $\alpha_{11} = -1.1088047$, $\alpha_{12} = -0.2276472$ ($\alpha_0^{L1_2} = \alpha_M^{FCC} = -1.79174723$).

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