

PARTIAL PAIR POTENTIALS IN LIQUID BINARY ALLOYS OF TRANSITION METALS

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Abstract: The Wills-Harrison partial effective pair potentials of liquid equiatomic Fe-Co, Fe-Ni, and Co-Ni alloys are calculated near their melting temperatures at different values of the probability that not only the diagonal coupling between d electrons in different atoms is possible. It is found that the first-minimum position and depth are being changed significantly with increase the magnitude of this probability for all potentials under consideration. The difference between Fe-Fe partial pair potentials at only diagonal coupling and at maximum possible non-diagonal one is the biggest and one between Ni-Ni partial potentials is the least among all potentials under study.

Key words: Transition metal, binary alloy, effective pair potential, Wills-Harrison approach, d -state coupling

1. INTRODUCTION

The description of the effective pair interaction in the transition metal is a hard task since the d -electron contribution to the potential energy in this case is non-pairwise in principle. There are a number of approximated forms for an effective pair potential in transition metals (Wills and Harrison, 1983; Moriarty, 1985; Foiles, 1985; Phuong et al., 1993). The model of Wills and Harrison (1983) (WH) is widely used to study the transition-metal melts (Hausleitner and Hafner, 1988; Regnaut, 1989; Bretonnet and Derouiche, 1991; Hausleitner et al., 1991; Dubinin et al., 2008; Dubinin, 2009). Recently, in the framework of the WH model we suggested the correction to the only diagonal coupling between d electrons in a pure transition metal and studied how this correction effects on the WH interatomic potentials in liquid Fe, Co, and Ni (Dubinin, 2012). Here, we apply this approach to binary mixtures of transition metals and study the partial WH interatomic potentials in liquid Fe-Co, Fe-Ni, and Co-Ni alloys.

2. THEORY

The foundation of the WH approximation is the suggestion that the wave functions of hybridized s - d

band may be approximated as a superposition of the plane waves and the d functions of a free atom. This means that conductive electrons may be divided into s and d ones.

The s electrons within the WH model behave like a nearly free and may be described in the nearly-free-electron (NFE) approximation with some perturbing pseudopotential as in the simple-metal theory. The difference is that one has to use the effective valence, z_s , instead of number of valence s electrons per ion. Due to the s - d hybridization, z_s is less than the number of valence s electrons in a free atom.

The d electrons are considered by Wills and Harrison as practically localized near the ion and the ion- d -electron potential in metal is described by using the muffin-tin (MT) potential (Andersen, 1975) in the atomic sphere (AS) approximation (Mackintosh and Andersen, 1979).

The shift of the d -electron energy of the metal with respect to the single atom in the second order of the perturbation theory is (Harrison and Froyen, 1980):

$$V_{dd'} = \sum_{\vec{k}} \frac{\langle d | \Delta | \vec{k} \rangle \langle \vec{k} | \Delta | d' \rangle}{e_d - e_{\vec{k}}} \quad (1)$$

where d and d' states are localized on different atoms; $|\vec{k}\rangle$ - the plane-wave function; e_d - the energy of the unperturbed d state; $e_{\vec{k}}$ - the plane-wave energy;

$$\Delta = \delta V - \langle d | \delta V | d \rangle \quad (2)$$

is the effective perturbing potential; δV - the difference between d -electron potentials in the metal and in the single atom.

Since Δ in eq. (1) is small enough, then the d -electron contribution into the density of states corresponds to a narrow peak. The width of the peak, W_d , may be calculated as a second moment of the d -states density using eq. (1):

$$W_d = \left(\frac{12}{N} \sum_{m=1}^N \sum_{\substack{l=1 \\ l \neq m}}^N V_d^2(\vec{r}_{ml}) \right)^{1/2} \quad (3)$$

where N - the number of atoms; $V_d(r)$ - the mean potential of the d - d interaction.

If to approximate the d -states density per ion by the rectangular model of Friedel (1969), it is possible to write the d -band energy per ion (Wills and Harrison, 1983):

$$E_b = -\frac{1}{2} z_d \left(\frac{10 - z_d}{10} \right) W_d \quad (4)$$

where z_d is the effective number of valence d electrons per ion.

Wills and Harrison had found also an additional energy term, E_c , due to the shift, ε_d , in the center of gravity of the d band due to nonorthogonality of d -like states:

$$E_c = z_d \varepsilon_d \quad (5)$$

$$\varepsilon_d = \frac{1}{2N} \sum_{m=1}^N \sum_{\substack{l=1 \\ l \neq m}}^N V_s(\vec{r}_{ml}) \quad (6)$$

Expressions (5) and (6) were obtained by using the perturbed d -state wave functions, to first order in Δ , written as follows:

$$|D\rangle = |d\rangle + \sum_{\vec{k}} |OPW_{\vec{k}}\rangle \frac{\langle \vec{k} | \Delta | d \rangle}{e_d - e_{\vec{k}}} \quad (7)$$

(where $|OPW_{\vec{k}}\rangle$ is the orthohonalized plane wave), and by using the overlap between perturbed d states at the muffin-tin zero at the d -state energy,

$$S_{dd'} = \delta_{dd'} + \sum_{\vec{k}} \frac{\langle d | \Delta | \vec{k} \rangle \langle \vec{k} | \Delta | d' \rangle}{(-k^2/2)^2} \quad (8)$$

Potentials $V_d(r)$ and $V_s(r)$ in MT-AS approximation are expressed as follows (hereafter in a.u.):

$$V_d(r) = \frac{r_d^3}{r^5} K_b \quad (9)$$

$$V_s(r) = \frac{r_d^6}{r^8} K_c \quad (10)$$

where K_b and K_c are some coefficients.

Wills and Harrison (1983) used the small argument expansion of the d -state radial function, which gives only diagonal coupling between d -electron states of different atoms with respect to the magnet quantum number, m (i.e. the coupling between d electrons with the same m only is possible). In this case, for the orbital quantum number $l = 2$, corresponded to transition metal,

$$K_b = \left(\sum_{m=-2}^2 \frac{y_m^2}{5} \right)^{\frac{1}{2}} \quad (11)$$

$$K_c = -2 \sum_{m=-2}^2 \frac{y_m x_m}{5} \quad (12)$$

where y_m and x_m are combinatoric coefficients:

$$y_m = -\frac{(-1)^m 180}{\pi(2+m)!(2-m)!} \quad (13)$$

$$x_m = -\frac{1}{8} \left(1 + \frac{4m^2 - 1}{9} \right) y_m \quad (14)$$

Eqs. (11) - (14) give:

$$K_b = \frac{28.06}{\pi} \quad (15)$$

$$K_c = \frac{225}{\pi^2} \quad (16)$$

In the work of Dubinin (2012) another representation of these coefficients was suggested:

$$K_b = \left[\frac{1}{5} \left(\left(1 - \frac{4p}{5} \right) y_0^2 + \left(2 - \frac{6p}{5} \right) (y_2^2 + y_1^2) + \frac{4p}{5} y_0(y_1 + y_2) + \frac{8p}{5} y_1 y_2 \right) \right]^{\frac{1}{2}} \quad (17)$$

$$K_c = -\frac{2}{5} \left[\left(1 - \frac{4p}{5} \right) y_0 x_0 + \left(2 - \frac{6p}{5} \right) (y_1 x_1 + y_2 x_2) + \frac{2p}{5} (y_0(x_1 + x_2) + x_0(y_1 + y_2)) + \frac{4p}{5} (y_1 x_2 + y_2 x_1) \right] \quad (18)$$

Here p is the probability that not only the diagonal coupling between d electrons in different atoms is possible; $y_m = y_{|m|}$ and $x_m = x_{|m|}$.

From the energy term E_c it is possible to obtain straightforwardly the corresponding contribution to the effective pair interaction:

$$\varphi_c(r) = z_d V_s(r) \quad (19)$$

Eq. (4) not gives the analogous possibility for obtaining the main contribution, $\varphi_b(r)$, to the d -electron-dependent part of the WH pair interaction. It was obtained approximately by means of expressing E_b in terms of nearest-neighbor matrix elements and by using its first variation from the bandwidth term (Wills and Harrison, 1983):

$$\begin{aligned} \delta(NE_b) &= -\frac{1}{2} z_d \left(\frac{10 - z_d}{10} \right) \sqrt{12} \times \\ &\times \left(\frac{1}{N} \sum_{m=1}^N \sum_{\substack{l=1 \\ l \neq m}}^N V_d^2(\vec{r}_{ml}) \right)^{-1/2} \times \\ &\times \sum_{m=1}^N \sum_{\substack{l=1 \\ l \neq m}}^N V_d(\vec{r}_{ml}) \delta V_d(\vec{r}_{ml}) = \\ &= -\frac{1}{2} z_d \left(\frac{10 - z_d}{10} \right) \sqrt{12} (\nu V_d^2(\alpha))^{-1/2} \times \\ &\times \sum_{m=1}^N \sum_{\substack{l=1 \\ l \neq m}}^N V_d(\alpha) \delta V_d(\vec{r}_{ml}) = \\ &= -\frac{1}{2} \sum_{m=1}^N \sum_{\substack{l=1 \\ l \neq m}}^N \delta \left[z_d \left(\frac{10 - z_d}{10} \right) \left(\frac{12}{\nu} \right)^{1/2} V_d(\vec{r}_{ml}) \right] \quad (20) \end{aligned}$$

where ν - the coordination number; α - the nearest-neighbor distance.

As a result,

$$\varphi_b(r) = -z_d \left(\frac{10 - z_d}{10} \right) \left(\frac{12}{\nu} \right)^{1/2} V_d(r) \quad (21)$$

For the binary system

$$V_{dij}(r) = \frac{(r_{di} r_{dj})^{3/2}}{r^5} K_b \quad (22)$$

$$V_{sij}(r) = \frac{(r_{di} r_{dj})^3}{r^8} K_c \quad (23)$$

where $i, j = 1, 2$.

The Wills-Harrison partial effective pair potentials are expressed as follows:

$$\varphi_{ijWH}(r) = \varphi_{ijNFE}(r) + \varphi_{dij}(r) \quad (24)$$

where $\varphi_{ijNFE}(r)$ and $\varphi_{dij}(r)$ are the contributions due to the s - and d -electron states, respectively.

The NFE term is

$$\varphi_{ijNFE}(r) = \frac{z_{si} z_{sj}}{r} + \frac{1}{8\pi^2 \rho} \int_0^\infty F_{ij}(q) \frac{\sin(qr)}{qr} q^2 dq \quad (25)$$

where ρ is the mean atomic density of the alloy; z_{si} - the effective number of valence s electrons per ion in the pure metal of the i -th kind; $F_{ij}(q)$ - partial energy-wavenumber characteristics:

$$F_{ij}(q) = -\frac{q^2 \omega_i(q) \omega_j(q)}{\pi \rho [(\varepsilon(q) - 1)^{-1} + 1 - f(q)]} \quad (26)$$

Here $\varepsilon(q)$ is the Hartree dielectric function; $f(q)$ - the exchange-correlation function (we take $f(q)$ in the approximation of Vashishta and Singwi, 1972); $\omega_i(q)$ - the form factor of the ion-electron potential for the bare ion of the i -th kind.

We use the Bretonnet and Silbert (1992) (BS) local model pseudopotential, $\omega_{BS}(r)$, written for the case of a mixture (Dubinin et al., 2007):

$$\omega_{iBS}(r) = \begin{cases} \sum_{n=1}^2 B_{ni} \exp\left(\frac{r}{na_i}\right), & r \leq R_{Ci} \\ -z_{si}/r, & r \geq R_{Ci} \end{cases} \quad (27)$$

$$\begin{aligned} \omega_{iBS}(q) &= 4\pi \rho \alpha_i^3 \left[\frac{B_{1i} J_{1i}(q)}{(1 + a_i^2 q^2)^2} + \frac{8B_{2i} J_{2i}(q)}{(1 + 4a_i^2 q^2)^2} \right] - \\ &- (4\pi \rho z_{si} / q^2) \cos(qR_{Ci}) \quad (28) \end{aligned}$$

where

$$B_{1i} = (z_{si} / R_{Ci}) [1 - 2a_i / R_{Ci}] \exp(R_{Ci} / a_i),$$

$$B_{2i} = (2z_{si} / R_{Ci}) [a_i / R_{Ci} - 1] \exp(0.5R_{Ci} / a_i),$$

$$J_{1i}(q) = 2 - \exp\left(-\frac{R_{Ci}}{a_i}\right) \left\{ \left[R_{Ci} \frac{1+a_i^2 q^2}{a_i} + 1 - a_i^2 q^2 \right] \times \right. \\ \left. \times \frac{\sin(qR_{Ci})}{a_i q} + \left[2 + \frac{R_{Ci}(1+a_i^2 q^2)}{a_i} \right] \cos(qR_{Ci}) \right\},$$

$$J_{2i}(q) = 2 - \exp\left(-\frac{R_{Ci}}{2a_i}\right) \left\{ \left[R_{Ci} \frac{1+4a_i^2 q^2}{2a_i} + 1 - 4a_i^2 q^2 \right] \times \right. \\ \left. \times \frac{\sin(qR_{Ci})}{2a_i q} + \left[2 + \frac{R_{Ci}(1+4a_i^2 q^2)}{2a_i} \right] \cos(qR_{Ci}) \right\}.$$

Here R_{Ci} and a_i - pseudo potential parameters.

The last term in the right-hand side of (24) consists of two parts: the first, $\varphi_{bij}(r)$, is due to the finite d -band width, and second, $\varphi_{cij}(r)$, arises from the shift of the d -band center:

$$\varphi_{dij}(r) = \varphi_{bij}(r) + \varphi_{cij}(r) \quad (29)$$

$$\varphi_{bij}(r) = -\bar{z}_d \left(\frac{10 - \bar{z}_d}{10} \right) \left(\frac{12}{\nu_{ij}} \right)^{1/2} \frac{(r_{di} r_{dj})^{3/2}}{r^5} K_b \quad (30)$$

$$\varphi_{cij}(r) = \bar{z}_d \frac{(r_{di} r_{dj})^3}{r^8} K_c \quad (31)$$

where $\bar{z}_d = c_1 z_{d1} + c_2 z_{d2}$; z_{di} - the effective number of valence d electrons per ion in the pure metal of the i -th kind: $z_{di} = z_i - z_{si}$, where z_i is the total number of valence electrons per i -th kind atom; r_{di} - the d -state radius of the free atom of the i -th kind; c_i - the concentration of the i -th kind component; ν_{ij} - the partial coordination numbers. We assume that ν for each pure Fe, Co, and Ni equal to 12. As a result all values of ν_{ij} for alloys under consideration are also taken equal to 12.

3. RESULTS AND DISCUSSIONS

The WH partial effective pair potentials of liquid equiatomic Fe-Co, Fe-Ni, and Co-Ni alloys near their melting temperatures at different values of p are considered. Values of r_{di} , z_{si} , R_{Ci} , and a_i are taken here the same as values of r_d , z_s , R_C , and a for corresponding pure metals from the works of Wills and Harrison (1983) for r_{di} and Jakse and Bretonnet (1995) for the others parameters. The mean atomic

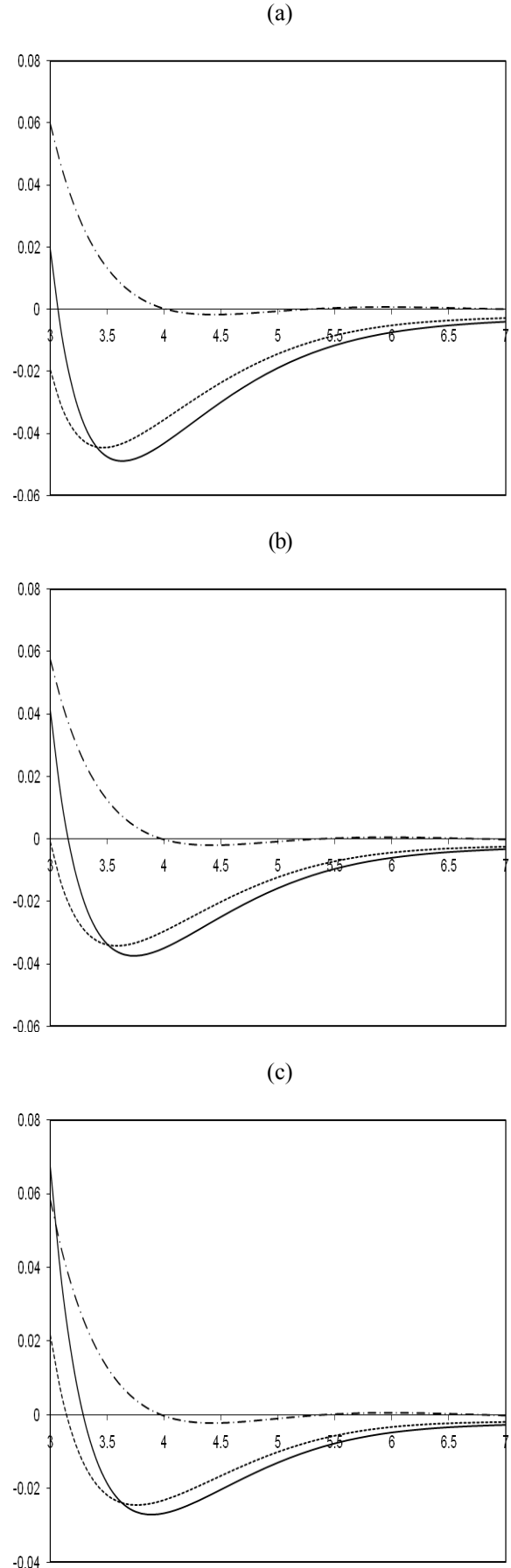
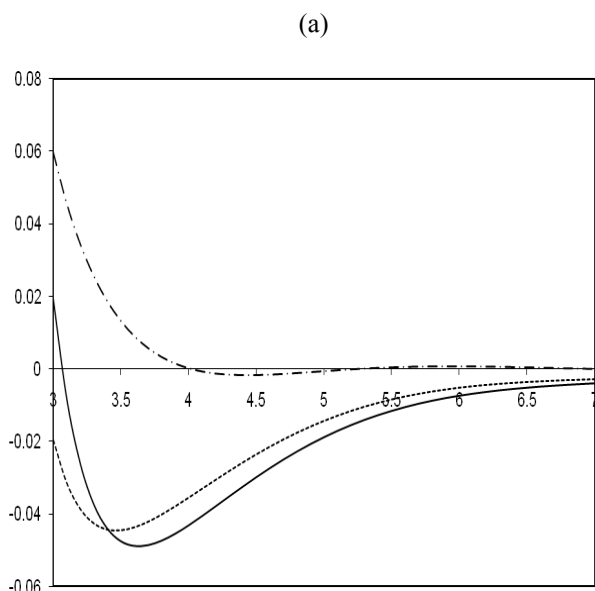
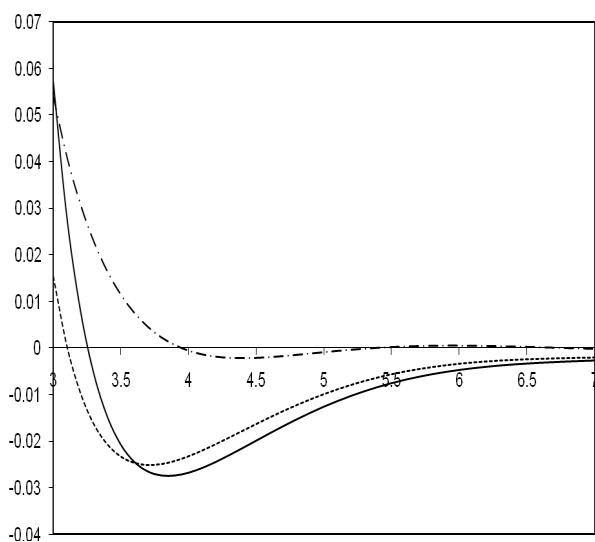


Fig. 1. The partial WH potentials Fe-Fe (a), Fe-Co (b), and Co-Co (c) in liquid equiatomic Fe-Co alloy near its melting temperature ($p=0$ – solid line; $p=0.5$ – dotted line; $p=1$ – dashed-dotted line).



(b)



(c)

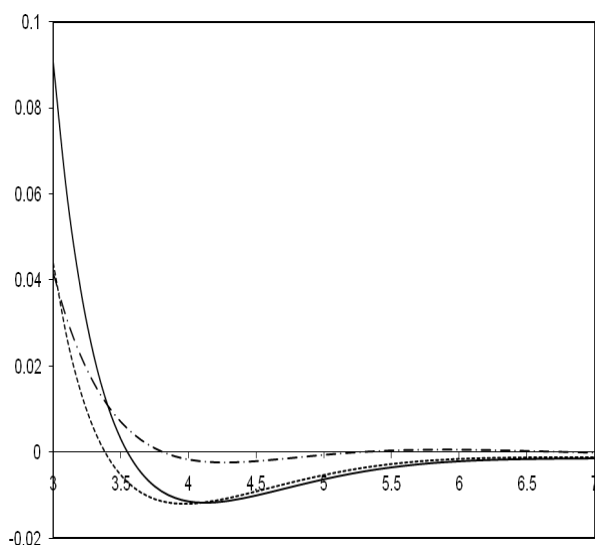
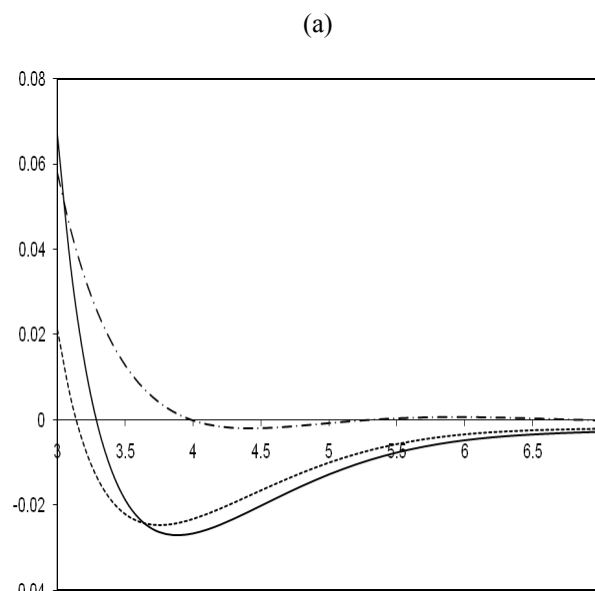
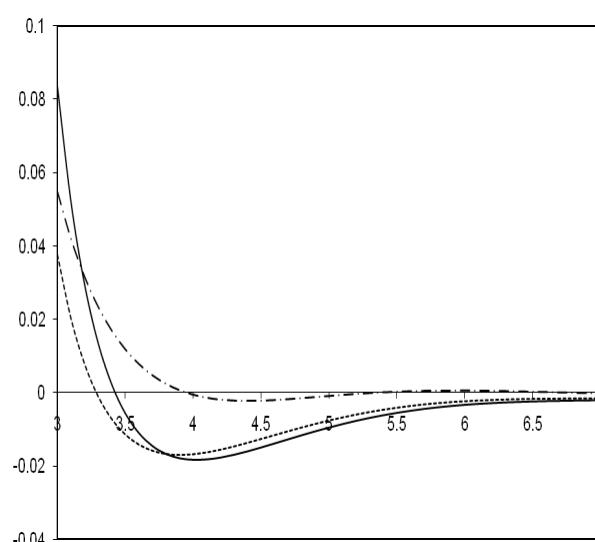


Fig. 2. The partial WH potentials Fe-Fe (a), Fe-Ni (b), and Ni-Ni (c) in liquid equiatomic Fe-Ni alloy near its melting temperature ($p=0$ – solid line; $p=0.5$ – dotted line; $p=1$ – dashed-dotted line).



(b)



(c)

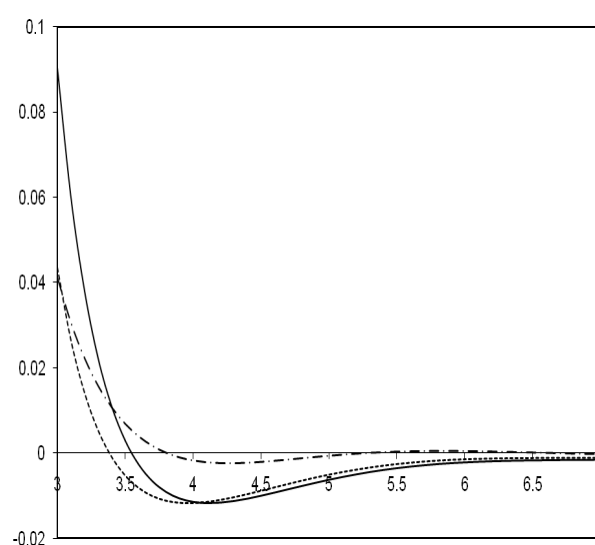


Fig. 3. The partial WH potentials Co-Co (a), Co-Ni (b), and Ni-Ni (c) in liquid equiatomic Co-Ni alloy near its melting temperature ($p=0$ – solid line; $p=0.5$ – dotted line; $p=1$ – dashed-dotted line).

density for each equiatomic alloy is calculated as an arithmetic average between experimental values of ρ obtained by Waseda (1981) for corresponding pure liquid metals. All needed input data are listed in Table 1.

Table 1. Input data for calculations

	Fe	Co	Ni
r_{di} (a.u.)	1.512	1.437	1.342
z_{si}	1.4	1.4	1.4
z_{di}	6.6	7.6	8.6
R_{Ci} (a.u.)	1.540	1.641	1.030
a_i (a.u.)	0.363	0.393	0.207
ρ (a.u.)	0.011199	0.011648	0.011732

Pair potentials obtained are presented in Figs.1-3. It is found that the depths of the first minimums are being reduced with increase the magnitude of p for all potentials under consideration. At the contrast of the pure-metal case (Dubinin, 2012), the first-minimum position of the partial pair potential has not a tendency to shift in a one direction only with changing p from 0 to 1. These positions shift to the left-hand side with change p from 0 to 0.5 and to the right-hand side with change p from 0.5 to 1. The difference between Fe-Fe partial potentials at $p=0$ and at $p=1$ is the biggest and one between Ni-Ni partial potentials is the least among all potentials under study.

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