Analytical methods for calculation of interatomic potentials through the data on the short-range order in alloys

Analytical methods for calculation of interatomic potentials through the data on the short-range order in alloys

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Abstract. Within the framework of the high-accuracy ring approximation elaborated by the authors (Chepulskii R V and Bugaev V N 1998a, b *J. Phys.: Condens. Matter* **10** 7309–26, 7327–48) in the context of the modified thermodynamic perturbation theory as applied to the lattice gas model, two methods are developed for calculation of the atomic interaction parameters in binary disordered alloys with Bravais crystal lattices through the data on the atomic short-range order (SRO)—the iteration method resulting in explicit analytical relationships and the variational method. Within both methods, the Fourier components of SRO parameters are used as initial data, thus, the most complete information on SRO in the alloy is taken into account. Both the iteration and variational methods permit us to calculate the atomic interaction parameters for an arbitrary number of the coordination shells as well as the Fourier components of the atomic interaction potentials. It is demonstrated that both methods have wide temperature–concentration intervals of applicability. The methods can be used under investigation not only of alloys, but also of other lattice systems (including low-dimensional ones, semiconductors and magnetics).

1. Introduction

The statistical-thermodynamic description of actual alloys requires the knowledge of adequate numerical information on the parameters of atomic interactions. One of the main methods for obtaining such information is based on the analysis of the atomic short-range order (SRO) data derived through the experiments on the diffuse scattering. In the framework of such an approach, the parameters of atomic interactions are calculated either by the analytical methods [1–12] or by simulations within the inverse Monte Carlo method [13].

In the recent works [14–17], in the framework of the ring approximation within the modified thermodynamic perturbation theory as applied to the lattice gas model, a new analytical method combining high accuracy and the simplicity of realization was developed for calculation of SRO parameters in binary disordered alloys with Bravais crystal lattices. The aim of the present paper is to resolve the inverse problem of calculation of the atomic interaction parameters of an alloy in the framework of the ring approximation through SRO data.

In section 2, as a first step in achievement of the present work's purpose, the solution of the inverse problem within the spherical model approximation (being the zero-order approximation within the approach developed in [15] and [16]) is obtained.

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In sections 3–5, two methods of resolving the inverse problem in the framework of the ring approximation—the iteration and variational ones—are developed. The numerical accuracies of both methods are examined.

In section 6, as an example, the advanced methods are applied in the case of $Ni_{0.89}Cr_{0.11}$ alloy.

In section 7, the obtained results are discussed.

2. Spherical model approximation

In the framework of the spherical model approximation, the expression for the Fourier transform α_k of the Warren–Cowley SRO parameters [18, 19] α_R in a disordered binary alloy A–B with a Bravais crystal lattice has the following form (see [14–16] and references therein):

$$\alpha_k = \left[1 + \frac{c(1-c)}{k_B T} \tilde{W}_k\right]^{-1} \tag{2.1}$$

where

$$\tilde{W}_k = \tilde{V}_k + \mu \tag{2.2}$$

$$\mu = 2(\Phi - \mu_A + \mu_B) \tag{2.3}$$

Φ is the injection potential, $\tilde{V}_k$ is the Fourier transform of the (pair) mixing potential V_R [20, 21],

$$\tilde{V}_k = \sum_R V_R \exp(-i\mathbf{k} \cdot \mathbf{R}) \qquad V_R = N^{-1} \sum_k \tilde{V}_k \exp(i\mathbf{k} \cdot \mathbf{R})$$

$$V_{R_1-R_2} = E_2^{AA}(\mathbf{R}_1 - \mathbf{R}_2) - 2E_2^{AB}(\mathbf{R}_1 - \mathbf{R}_2) + E_2^{BB}(\mathbf{R}_1 - \mathbf{R}_2) \tag{2.4}$$

$$\Phi = [E_1^A(\mathbf{R}) - E_1^B(\mathbf{R})] + \sum_{R'} [E_2^{AB}(\mathbf{R} - \mathbf{R}') - E_2^{BB}(\mathbf{R} - \mathbf{R}')]$$

$E_1^\alpha(\mathbf{R})$ is the self-energy of an α-type atom at the site $\mathbf{R}$ associated with the presence of an external (with respect to the alloy) field, $E_2^{\alpha_1\alpha_2}(\mathbf{R}_1 - \mathbf{R}_2)$ is the energy of the pairwise interaction of α_1- and α_2-type atoms occupying the sites $\mathbf{R}_1$ and $\mathbf{R}_2$, respectively, μ_A and μ_B are the chemical potentials of A and B components of the alloy, respectively, c is the concentration of A component, k_B is the Boltzmann constant, T is the absolute temperature. Hereafter, the symbols $\sum_R$ and $\sum_k$ are used, accordingly, for the designation of the summation over all N crystal lattice sites (with the radius-vectors $\mathbf{R}$) and over all N points distinguished by the cyclic boundary conditions within the corresponding first Brillouin zone.

Let us rewrite (2.1), taking account of (2.2), as follows

$$\tilde{V}_k + \mu = \frac{k_B T}{c(1-c)} [(\alpha_k)^{-1} - 1]. \tag{2.5}$$

Integrating the right and left parts of the equality (2.5) over the first Brillouin zone and using the condition [20, 21]

$$\tilde{V}_{R=0} = 0 \tag{2.6}$$

we obtain

$$\mu = \mu^{SM} = \frac{k_B T}{c(1-c)} (Q - 1) \tag{2.7}$$

where

$$Q = N^{-1} \sum_q (\alpha_q)^{-1}. \tag{2.8}$$

Substituting (2.7) into (2.5), we have

$$\tilde{V}_k = \tilde{V}_k^{SM} = \frac{k_B T}{c(1-c)} [(\alpha_k)^{-1} - Q]. \tag{2.9}$$

The integration of the equality (2.9) with the factor $\exp(\mathrm{i}\mathbf{k} \cdot \mathbf{R})$ over the first Brillouin zone yields

$$\tilde{V}_R = V_R^{SM} = \frac{k_B T}{c(1-c)} \left[N^{-1} \sum_k (\alpha_k)^{-1} \exp(\mathrm{i}\mathbf{k} \cdot \mathbf{R}) - \delta_{R,0} Q \right] \tag{2.10}$$

where

$$\delta_{R,0} = B^{-1} \sum_k \exp(\mathrm{i}\mathbf{k} \cdot \mathbf{R}) = \begin{cases} 1 & \text{if } \mathbf{R} = 0 \\ 0 & \text{if } \mathbf{R} \neq 0. \end{cases} \tag{2.11}$$

The expressions (2.7)–(2.10) permit us to calculate the quantity μ (2.3) as well as the mixing potential and its Fourier transform through SRO data in the framework of the spherical model approximation. Notice that the solution of the inverse problem as to the mixing potential for 'nonzero' coordination shells obtained in the framework of the spherical model approximation coincides (see (2.10)) with the corresponding solution obtained within the Krivoglaz approximation [1, 2, 22] or, respectively, within the Krivoglaz–Clapp–Moss one [3, 4], setting the corresponding normalizing multiplier equal to unity. However, within the spherical model approximation, in contrast to the cases of both denoted approximations, the general condition (2.6) is satisfied.

3. Ring approximation

With the aim of resolving the inverse problem in the framework of the ring approximation, it is convenient to present the corresponding expression for α_k [14–16] in the following form [23]

$$L_k = (\alpha_k)^{-1} + \Psi_k[L_k] \tag{3.1}$$

where the functional Ψ_k on the function L_k

$$L_k = 1 + \frac{c(1-c)}{k_B T} W_k \tag{3.2}$$

is determined by the expression

$$\Psi_k[L_k] = c_1 - N^{-1} \sum_q \frac{1}{L_q} \left(c_2 - \frac{c_3}{L_{k-q}} \right) \tag{3.3}$$

where

$$c_1 = \frac{1 - 2c(1-c)}{2c(1-c)} \qquad c_2 = \frac{1 - 3c(1-c)}{c(1-c)} \qquad c_3 = \frac{(1-2c)^2}{2c(1-c)}. \tag{3.4}$$

Note that, setting $\Psi_k[L_k] \equiv 0$ in the expression (3.1), we arrive (see (2.1) and (3.2)) at the spherical model approximation:

$$L_k^{SM} = (\alpha_k)^{-1} \tag{3.5}$$

and, thus, $\Psi_k[L_k]$ is the correction within the ring approximation to the spherical model one.

Integrating the right and the left parts of the equality (3.1) over the first Brillouin zone with the factor $\exp(\mathrm{i}\boldsymbol{k} \cdot \boldsymbol{R})$, we obtain

$$L_R = L_R^{SM} + \delta_{R,0}(c_1 - c_2 F_{R=0}) + c_3(F_R)^2 \tag{3.6}$$

where

$$L_R = N^{-1} \sum_k L_k \exp(\mathrm{i}\boldsymbol{k} \cdot \boldsymbol{R}) \tag{3.7}$$

$$L_R^{SM} = N^{-1} \sum_k L_k^{SM} \exp(\mathrm{i}\boldsymbol{k} \cdot \boldsymbol{R}) = N^{-1} \sum_k (\alpha_k)^{-1} \exp(\mathrm{i}\boldsymbol{k} \cdot \boldsymbol{R}) \tag{3.8}$$

$$F_R = N^{-1} \sum_k (L_k)^{-1} \exp(\mathrm{i}\boldsymbol{k} \cdot \boldsymbol{R}). \tag{3.9}$$

It should be noted that, from (3.6), taking account of (3.2), one can conclude that the correction for the mixing potential within the ring approximation to the spherical model one is always positive (or equal to zero). Really, integrating (3.2) over the first Brillouin zone with the factor $\exp(\mathrm{i}\boldsymbol{k} \cdot \boldsymbol{R})$ under $\boldsymbol{R} \neq 0$, we obtain

$$L_R = \frac{c(1-c)}{k_b T} W_r \qquad (\boldsymbol{R} \neq 0). \tag{3.10}$$

Substituting (3.10) into (3.6), we have

$$V_R = V_R^{SM} + \frac{k_B T}{2} \left[\frac{1-2c}{c(1-c)} F_R \right]^2 \qquad (\boldsymbol{R} \neq 0) \tag{3.11}$$

from where the above statement becomes evident.

Under resolution of the inverse problem, one should consider the equality (3.1) (or (3.6)) as an equation on the unknown function L_k (or L_R) at a given function α_k. If the solution of this equation has been found, the quantities μ, $\tilde{V}_k$ and $\tilde{V}_R$ can be expressed explicitly in terms of this solution. Really, integrating the equality (3.2) over the first Brillouin zone and taking into account (2.2) and (2.6), we obtain

$$\mu = \frac{k_B T}{c(1-c)}(L_{R=0} - 1). \tag{3.12}$$

Substituting (3.12) into (3.2), we arrive at the following expression

$$V_k = \frac{k_B T}{c(1-c)}(L_k - L_{R=0}) \tag{3.13}$$

the integrating of which with the factor $\exp(\mathrm{i}\boldsymbol{k} \cdot \boldsymbol{R})$ over the first Brillouin zone yields

$$V_R = \frac{k_B T}{c(1-c)}(L_R - \delta_{R,0} L_{R=0}). \tag{3.14}$$

Thus, the inverse problem in the framework of the ring approximation is reduced to the solving of the equations (3.1) and (3.6). Since the exact solving of these equations seems to be impossible due to their non-linear integral character, in the following two sections we develop two corresponding approximate methods—the iteration and variational ones.

4. Iteration method

The simplest approximate solutions of the equation (3.1) are, first, the expression (3.5) corresponding to the spherical model approximation and, second, the following expression obtained as a result of the first iteration of (3.1):

$$L_k^{IT} = (\alpha_k)^{-1} + \Psi_k[(\alpha_k)^{-1}] = (\alpha_k)^{-1} + c_1 - c_2\alpha_{R=0} + \tilde{c}_3 N^{-1} \sum_q \alpha_q \alpha_{k-q}. \tag{4.1}$$

Substituting (4.1) into (3.12)–(3.14), we obtain, accordingly

$$\mu^{IT} = \mu^{SM} + \frac{k_B T}{c(1-c)} [c_1 - c_2\alpha_{R=0} + \tilde{c}_3(\alpha_{R=0})^2] \tag{4.2}$$

$$V_k^{IT} = V_k^{SM} + \frac{k_B T}{2} \left[\frac{1-2c}{c(1-c)}\right]^2 \left[N^{-1} \sum_q \alpha_q \alpha_{k-q} - (\alpha_{R=0})^2\right] \tag{4.3}$$

$$V_R^{IT} = V_R^{SM} + \frac{k_B T}{2} \left[\frac{1-2c}{c(1-c)}\right]^2 [(\alpha_R)^2 - \delta_{R,0}(\alpha_{R=0})^2]. \tag{4.4}$$

Taking into account the condition [3–5, 15, 16, 24–26]

$$\alpha_{R=0} = 1 \tag{4.5}$$

the expressions (4.1)–(4.4) take the following form

$$L_k^{IT} = (\alpha_k)^{-1} + \tilde{c}_3 \left(N^{-1} \sum_q \alpha_q \alpha_{k-q} - 1\right) \tag{4.6}$$

$$\mu^{IT} = \mu^{SM} \tag{4.7}$$

$$V_k^{IT} = V_k^{SM} + \frac{k_B T}{2} \left[\frac{1-2c}{c(1-c)}\right]^2 \left(N^{-1} \sum_q \alpha_q \alpha_{k-q} - 1\right) \tag{4.8}$$

$$V_R^{IT} = V_R^{SM} + \frac{k_B T}{2} \left[\frac{1-2c}{c(1-c)}\right]^2 [(\alpha_R)^2 - \delta_{R,0}]. \tag{4.9}$$

It is evident (see (4.1)) that the closer to one another the results of the spherical model and the ring approximations, the higher the numerical accuracy of the described iteration method. Thus, on the basis of the analysis performed in [16], one may suppose the rise of the numerical accuracy of the iteration method, when the composition approaches the equiatomic value, with increase of an effective radius of atomic interactions and under the moving away from the point of phase transition, because just in these cases the results of the ring and spherical model approximations draw close together.

To examine the numerical accuracy of the approximation of the exact solution of the equation (3.1) by the expression (3.5) (within the spherical model approximation) as well as by the expression (4.1) (within the iteration method), we considered four model cases corresponding to the short-range atomic interactions: $c = 0.1$ and 0.25 at $V_1 > 0$, $V_2 = 0$ and $V_1 > 0$, $V_2 = -0.5V_1$ (V_s is the mixing potential on the sth coordination shell of the f.c.c. crystal lattice; in all cases $V_s = 0$ for $s > 2$). In every considered case, for a given temperature, the function α_k (and, respectively, α_R) was calculated within the ring approximation by the use of the formula (3.1), under the given corresponding mixing potential. Using the obtained function α_k, by means of (2.10) and (4.9) in the framework of, accordingly, the spherical model approximation and iteration method, the mixing potential was recalculated and compared with the initial potential. In figures 1–4 for all four cases considered, the results of such calculations are presented within the temperature interval
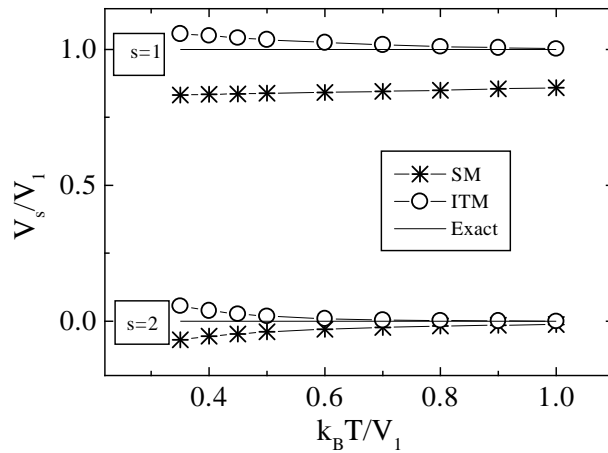
Figure 1. The results of the calculations of the values of the mixing potential V_s for the first two coordination shells ($s = 1, 2$) in the framework of the spherical model approximation (SM) and iteration method (ITM) on the basis of SRO data obtained within the ring approximation (3.1) in the case $c = 0.1$, $V_1 > 0$ ($V_s = 0$ for $s > 1$) in the temperature interval $[T_0, 2T_0]$ (where $k_B T_0/V_1 = 0.35(5)$ is the reduced temperature of order–disorder phase transition calculated in [16] by the direct Monte Carlo method).
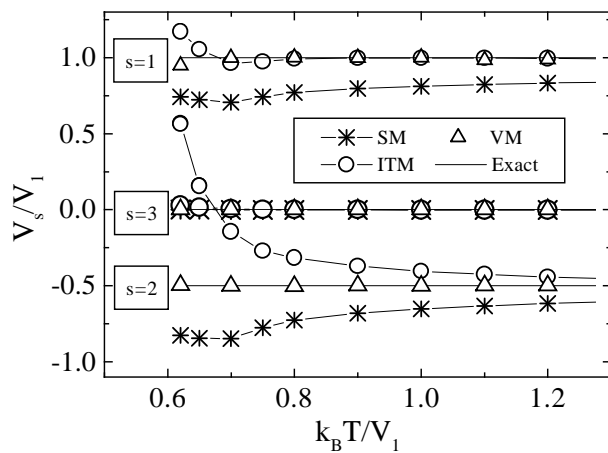

Figure 2. The same as in figure 1, but for $s = 1, 2, 3$ in the case $c = 0.1$, $V_1 > 0$, $V_2 = -0.5V_1$ ($V_s = 0$ for $s > 2$). 'VM' is the designation of the results of the calculations in the framework of the variational method; $k_B T_0/V_1 = 0.615(5)$.

$[T_0, 2T_0]$, where T_0 is the temperature of the order–disorder phase transition calculated by the Monte Carlo method in [16]. The accuracies of approximate solutions obtained in the framework of the spherical model approximation and iteration method can be judged by the degree of deviation of the corresponding dependencies from the exact solutions known beforehand accordingly to the applied procedure.

From the data presented in figures 1–4, it follows that, at $c = 0.25$ in both considered cases, the spherical model approximation as well as the iteration method yield adequate results (with the relative error less than 10%) almost within the entire considered temperature
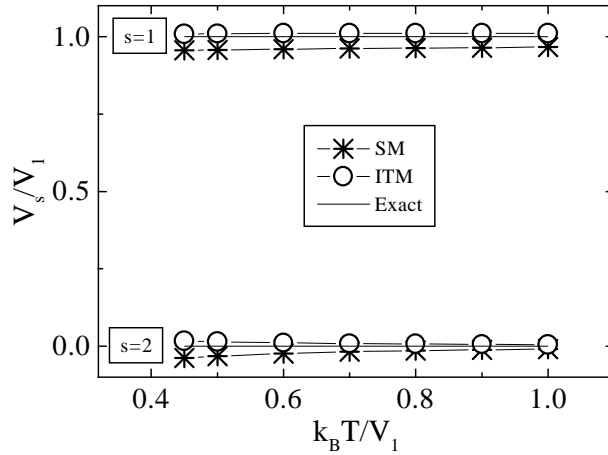
Figure 3. The same as in figure 1 but in the case $c = 0.25$, $V_1 > 0$ ($V_s = 0$ for $s > 1$); $k_B T_0 / V_1 = 0.449(1)$.
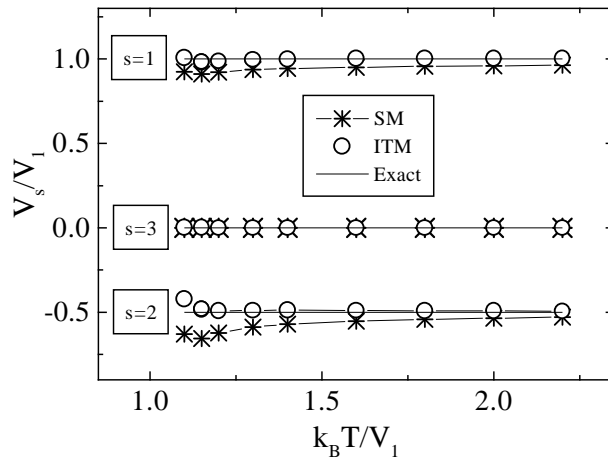
Figure 4. The same as in figure 2 but in the case $c = 0.25$, $V_1 > 0$, $V_2 = -0.5V_1$ ($V_s = 0$ for $s > 2$); $k_B T_0 / V_1 = 1.095(5)$.

interval except for an immediate vicinity of T_0. Under the concentration decrease, the lowering of the numerical accuracies of both methods takes place. As a result, at $c = 0.1$ and $V_1 > 0$, $V_2 = -0.5V_1$, the iteration method and the spherical model approximation become inadequate in the temperature intervals $[T_0, 1.6T_0]$ and $[T_0, 2T_0]$, respectively. At $c = 0.1$ and $V_1 > 0$, $V_2 = 0$ the iteration method is adequate and the spherical model approximation is inadequate almost within the entire considered temperature intervals.

Thus, the performed analysis demonstrates that the approximation of the exact solution of the equations (3.1) and (3.6) obtained within the spherical model approximation and the iteration method may be rough in the case of a dilute alloy with the short-range atomic interactions, as well as in the case of an alloy under the temperatures close to the temperature of phase transition. Unfortunately, it was revealed that, generally, successive iterations as in (4.1) do not lead to increase of the numerical accuracy of the approximate solution of

these equations due to the divergence of the corresponding iteration procedure. That is why the next section is devoted to the development of the variational method for the calculation of the corrections to a solution obtained within the iteration method.

5. Variational method

Let us present the solution of the equations (3.1) and (3.6) in the following form

$$L_k = L_k^{IT} + \delta L_k \qquad L_R = L_R^{IT} + \delta L_R \tag{5.1}$$

where L_k^{IT} is determined in (4.1),

$$L_R^{IT} = N^{-1} \sum_k L_k^{IT} \exp(i k \cdot R) \tag{5.2}$$

$$\delta L_R = N^{-1} \sum_k \delta L_k^{IT} \exp(i k \cdot R). \tag{5.3}$$

Substituting (5.1) into (3.6), we arrive at the equation in the function δL_R:

$$\delta L_R = \delta_{R,0} c_2 (\alpha_{R=0} - F_{R=0}) - \tilde{c}_3 [(\alpha_r)^2 - (F_R)^2] \tag{5.4}$$

where, according to (3.9) and (5.1),

$$F_R = N^{-1} \sum_k (L_k^{IT} + \delta L_k)^{-1} \exp(i k \cdot R). \tag{5.5}$$

The numerical consideration performed in section 4 demonstrates the tendency of quick decrease of the error of the mixing potential calculations with increase of the radius of the coordination shell within both the spherical model approximation and the iteration method. One can also suggest the same tendency for the quantity (see (4.4))

$$V_R^{IT} - V_R^{SM} = \frac{k_B T (1 - 2c)^2}{2[c(1 - c)]^4} (\varepsilon_R)^2 \qquad (R \neq 0) \tag{5.6}$$

due to the quick (outside the critical region) reduction of the absolute value of the correlation function $\varepsilon_R = c(1 - c)\alpha_R$ with distance. Thus, it is reasonable to suppose that the solution of the equation (5.4)—the quantity δL_R—also decreases quickly in magnitude with the growth of $|R|$. The invalidity of this assumption one may expect (see (5.6)) only in an immediate vicinity of the critical temperature (owing to the corresponding abrupt increase of the effective radius of interatomic correlations) and/or in the case of a dilute alloy.

Starting from the denoted assumption and using the definition (5.3), let us represent the quantity δL_k in the following approximate form

$$\delta L_k = \sum_R \delta L_R \exp(-i k \cdot R) = \sum_{s=0}^{\infty} \delta L_s Z_s(k) \approx \sum_{s=0}^{S_L} \delta L_s Z_s(k) \tag{5.7}$$

where s is the number of the coordination shell,

$$\delta L_s = \delta L_{R_s} \tag{5.8}$$
$$Z_s(k) = \sum_{R_s} \exp(-i k \cdot R_s) \tag{5.9}$$

R_s is the radius-vector of the site belonging to the sth coordination shell, s_L is the number of the coordination shell such that the quantity δL_s at $s > s_L$ is negligibly small:

$$\delta L_s = 0 \qquad s > s_L. \tag{5.10}$$

It should be noted that in the case of 'noncentrality' of the coordination shell, i.e. when the total number of the sites belonging to the shell can be divided into a number of symmetrically

unequivalent groups (with the different values of the mixing potential for the sites from different groups) [20, 21], *unequal* values of the numbering index s should be appropriated to the sites belonging to different groups.

Substituting (5.7) into (5.4), we have

$$\delta L_s = \delta_{s,0} c_2 (\alpha_{s=0} - F_0) - \tilde{c}_3 [(\alpha_s)^2 - (F_s)^2] \tag{5.11}$$

where $s = 0, 1, 2, \ldots,$

$$\alpha_s = \alpha_{R_s} \tag{5.12}$$

$$F_s = N^{-1} \sum_{\boldsymbol{k}} \left[L_{\boldsymbol{k}}^{IT} + \sum_{s=0}^{S_L} \delta L_s Z_s(\boldsymbol{k}) \right]^{-1} \exp(\mathrm{i} \boldsymbol{k} \cdot \boldsymbol{R}_s). \tag{5.13}$$

The quantities δL_s ($s = 0, 1, 2, \ldots, s_L$—see (5.10)) can be determined with any required accuracy by means of their variation to find the minimum of the sum of the absolute values of the differences between the left- and right-hand sides of the equation (5.11):

$$\sum_{s=0}^{s_{eq}} |\delta L_s - \delta_{s,0} c_2 (\alpha_{s=0} - F_0) + \tilde{c}_3 [(\alpha_s)^2 - (F_s)^2]| \tag{5.14}$$

taking into account (5.10) and (5.13). Under the minimization of the expression (5.14), the quantities δL_s ($s = 0, 1, 2, \ldots, s_L$), should be varied near the zero value to obtain the solution close to those derived within the iteration method. The values of s_L should be chosen step by step equal to $0, 1, 2, \ldots$ as long as convergence of the results with the increase of s_L (with required accuracy) is achieved. For every given s_L, it is necessary also to achieve convergence of the results with the increase of the number $s_{eq} \geqslant s_L$ of equations being used in the described variational method. Note that, as revealed in calculations (see below), to achieve a desired high accuracy, it is sufficient to set $s_{eq} = s_L$ and to vary L_s corresponding only to those coordination shells for which the differences between the spherical model approximation and iteration method results are large.

After determination of the quantities δL_s, the values of μ, $V_{\boldsymbol{k}}$ and V_R can be calculated through the following relationships (see (3.12)–(3.14)):

$$\mu = \mu^{IT} + \frac{k_B T}{c(1-c)} \delta L_{s=0} \tag{5.15}$$

$$V_{\boldsymbol{k}} = V_{\boldsymbol{k}}^{IT} + \frac{k_B T}{c(1-c)} \sum_{s=0}^{S_L} \delta L_s Z_s(\boldsymbol{k}) \tag{5.16}$$

$$V_s = V_s^{IT} + \frac{k_B T}{c(1-c)} (\delta L_s - \delta_{s,0} \delta L_{s=0}). \tag{5.17}$$

To examine the adequacy of the determined values of μ, $V_{\boldsymbol{k}}$ and V_R, one should substitute them into (3.1) and compare the resulting functions $\alpha_{\boldsymbol{k}}$ and α_R with the initial corresponding functions $\alpha_{\boldsymbol{k}}$ and α_R that were used for determination of μ, $V_{\boldsymbol{k}}$ and V_R.

As an example, we applied the variational method in the model case (among those considered in section 4) in which the low accuracy of the iteration method was demonstrated in a wide temperature interval: $c = 0.1$, $V_1 > 0$, $V_2 = -0.5V_1$ ($V_s = 0$ for $s > 2$). As follows from figure 2, the results obtained within the variational method exhibit high numerical accuracy for all considered temperatures. It should be noted that at the value of the reduced temperature $k_B T / V_1 = 0.62$ (i.e. even in the immediate vicinity of the phase transition temperature—see figure 2) the variation of only eight parameters was required, whereas at $k_B T / V_1 \geqslant 0.7$ the variation of three parameters turned out to be sufficient.
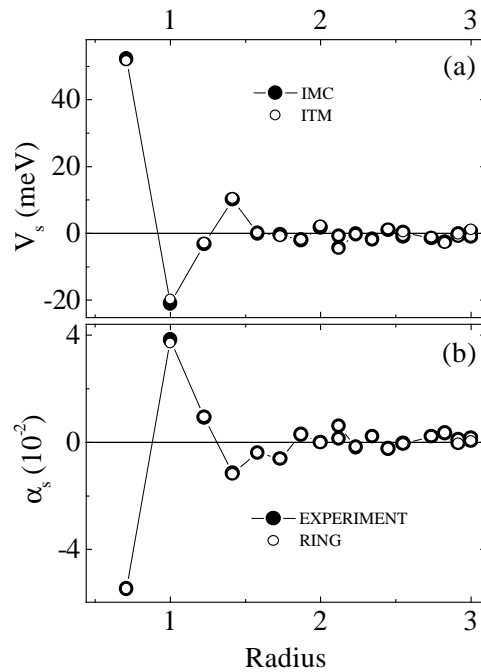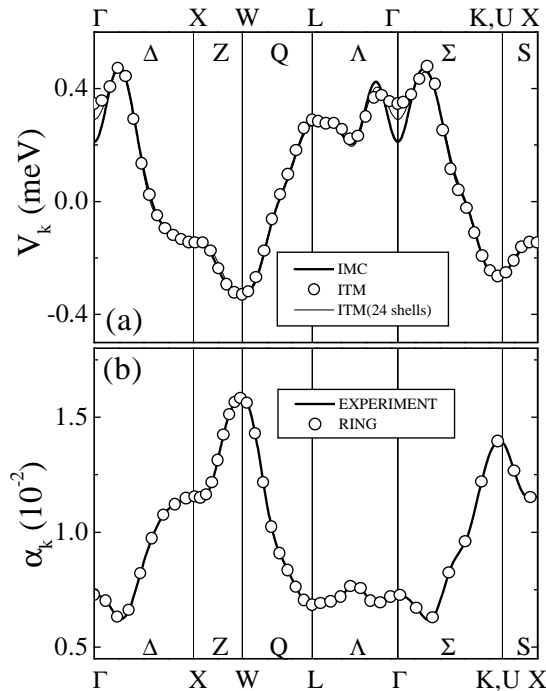
Figure 5. In the case of $Ni_{0.89}Cr_{0.11}$ at $T = 833$ K (a) the values of the mixing potential for 17 coordination shells calculated in the framework of the inverse Monte Carlo (IMC) and iteration (ITM) methods; (b) the values of SRO parameters obtained experimentally (EXPERIMENT) and in the framework of the ring approximation (RING) by the use of the general formula (3.1) at substitution of the mixing potential values calculated within the iteration method. The radius of coordination shells is given in units of lattice parameter.

Thus, in the considered case, the above assumption about the quick convergence of the variational method with an increase of the number of variable parameters is justified outside an immediate vicinity of the phase transition temperature. Therefore, even in such an 'unprofitable' case as considered (characterized by a low numerical accuracy of the iteration method), the variational method permits us to obtain results of high numerical accuracy in a wide temperature interval under relatively small time consumptions.

6. Case of $Ni_{0.89}Cr_{0.11}$

With the aim of application of the methods advanced in the previous sections in the case of actual alloys, we took advantage of the data on SRO obtained by Schweika and Haubold [27] on the basis of the experimental data for the f.c.c. alloy $Ni_{0.89}Cr_{0.11}$ at $T = 833$ K. In tables 1 and 2, the corresponding values of the mixing potential for the first 30 coordination shells and of its Fourier transform in the high-symmetry points within the first Brillouin zone calculated within the spherical model and recently elaborated Tokar–Masanskii–Grishchenko [9, 10]† approximations as well as within the iteration and variational (with six variable

† Note that the expressions derived in the framework of the Tokar–Masanskii–Grishchenko approximation for the mixing potential (a) for the second and third coordination shells are identical to the corresponding expressions obtained within the iteration method (see (4.9)) and (b) for the coordination shells beginning with the fourth one are identical to the corresponding expressions obtained within the spherical model approximation (see (2.10)) [9, 10, 23].

Figure 6. The dependencies on the wavevector along the high-symmetry directions [37] within the first Brillouin zone of (a) the Fourier transforms of the mixing potential obtained within the inverse Monte Carlo (IMC) and iteration (ITM) methods; (b) the Fourier transforms of SRO parameters calculated experimentally (EXPERIMENT) and in the framework of the ring approximation (RING) by the use of the general formula (3.1) at substitution of the mixing potential values calculated within the iteration method. The designation 'ITM (24 shells)' corresponds to the accounting of the values of the mixing potential calculated in the framework of the iteration method only for 24 coordination shells in a calculation of the Fourier transform.

parameters) methods are presented. The corresponding results of calculations performed by Schweika and Haubold [27] and Finel [12] in the framework of the inverse Monte Carlo and cluster variation methods, respectively, are also presented in these tables. In figure 5, the values of the mixing potential for the first 17 coordination shells calculated within the inverse Monte Carlo and iteration methods are given in graphical form as well as the values of SRO parameters obtained experimentally and within the ring approximation by the use of the general formula (3.1) at substitution of the mixing potential values calculated within the iteration method.

In figure 6, the dependence of the Fourier transform of the mixing potential obtained within the inverse Monte Carlo and iteration methods on the wavevector is presented along the high-symmetry directions within the first Brillouin zone. The same dependence of the Fourier transform of SRO parameters calculated both on the basis of the experimental data and in the framework of the ring approximation by the use of the general formula (3.1) on substitution of the mixing potential values obtained within the iteration method are presented in this figure as well.

Table 1 indicates the closeness of the values of the mixing potential calculated in the framework of the iteration and variational methods. This fact as well as the sufficiency to vary only six parameters prove the high convergence of the variational method on increase

Table 1. The values of the mixing potential V_R for the first 30 coordination shells calculated in the framework of the spherical model (SM) and Tokar–Masanskii–Grishchenko (TMG) [9, 10] approximations as well as within the iteration (ITM), variational with six variable parameters (VM), inverse Monte Carlo (IMC) and cluster variation (ICVM) methods on the basis of the data of Schweika and Haubold [27] on SRO in $Ni_{0.89}Cr_{0.11}$ at $T = 833$ K. All quantities are given in meV; lmn are the Miller indices of the vector R; the radii of coordination shells are given in units of lattice parameter.

Shell	lmn	Radius	SM	ITM	VM	IMC[a]	TMG	ICVM[b]
1	110	0.707	44.77	51.59	51.44	52.2(6)	53.55	54.4(12)
2	200	1.000	−23.07	−19.76	−20.57	−21.0(8)	−19.76	−20.0(8)
3	211	1.225	−3.10	−2.91	−2.91	−3.2(4)	−2.91	−3.2(8)
4	220	1.414	10.21	10.51	10.47	10.2(6)	10.21	11.2(8)
5	310	1.581	0.04	0.08	0.07	0.0(4)	0.04	
6	222	1.732	−0.92	−0.84	−0.85	−0.4(10)	−0.92	
7	321	1.871	−1.93	−1.91	−1.91	−2.0(4)	−1.93	
8	400	2.000	2.27	2.27	2.27	1.8(10)	2.27	
9	411	2.121	−0.81	−0.80	−0.80	−0.8(6)	−0.81	
	330		−4.70	−4.62	−4.62	−4.4(6)	−4.70	
10	420	2.236	−0.37	−0.36	−0.36	−0.2(6)	−0.37	
11	332	2.345	−1.93	−1.91	−1.91	−1.8(4)	−1.93	
12	422	2.450	1.19	1.20	1.20	1.0(6)	1.19	
13	431	2.550	−0.76	−0.76	−0.76	−1.0(4)	−0.76	
	510		0.39	0.39	0.39	0.2(6)	0.39	
14	521	2.739	−1.20	−1.19	−1.19	−1.4(4)	−1.20	
15	440	2.828	−2.95	−2.92	−2.92	−2.6(6)	−2.95	
16	433	2.916	−0.95	−0.95	−0.95	−0.8(6)	−0.95	
	530		−0.19	−0.19	−0.19	−0.2(4)	−0.19	
17	442	3.000	−1.00	−0.99	−0.99	−1.0(6)	−1.00	
	600		1.11	1.11	1.11	0.6(10)	1.11	
18	532	3.082	1.84	1.85	1.85	1.6(4)	1.84	
	611		1.26	1.26	1.26	1.0(6)	1.26	
19	620	3.162	−0.42	−0.41	−0.41	−0.6(8)	−0.42	
20	541	3.240	−0.03	−0.03	−0.03	−0.2(4)	−0.03	
21	622	3.317	−0.02	−0.02	−0.02	−0.2(6)	−0.02	
22	631	3.391	−0.17	−0.17	−0.17	−0.4(4)	−0.17	
23	444	3.464	−0.14	−0.13	−0.13	0.0(10)	−0.14	
24	550	3.536	−2.46	−2.44	−2.44	−2.2(6)	−2.46	
	543		0.42	0.42	0.42	0.2(4)	0.42	
	710		0.88	0.88	0.88		0.88	
25	640	3.606	−0.03	−0.03	−0.03		−0.03	
26	633	3.674	0.74	0.74	0.74		0.74	
	255		0.06	0.06	0.06		0.06	
	721		0.25	0.25	0.25		0.25	
27	642	3.742	0.34	0.34	0.34		0.34	
28	730	3.808	−0.08	−0.08	−0.08		−0.08	
29	732	3.937	−0.13	−0.13	−0.13		−0.13	
	651		−0.23	−0.23	−0.23		−0.23	
30	800	4.000	0.22	0.22	0.22		0.22	

[a] The simulation data of Schweika and Haubold from [27].
[b] The cluster-variation method data of Finel from [12].

of the number of varied parameters in the considered case. Due to the denoted closeness of the values of the mixing potential calculated within the iteration and variational methods, only the data corresponding to the iteration method are presented in figures 5 and 6.

The closeness (see figures 5(b) and 6(b)) of the corresponding 'experimental' values of SRO parameters (which are the initial data both for the iteration and variational methods) and the values obtained in the framework of the ring approximation by the use of the general formula (3.1) on substitution of the mixing potential values obtained within the iteration method testifies that, on solving the inverse problem even in the framework of the simple iteration method, we nearly achieve the accuracy of the ring approximation.

Accepting the results of the inverse Monte Carlo method as a standard, on the basis of the data presented in tables 1, 2 and figures 5(a), 6(a), one may conclude that the results of the iteration and variational methods are of a high numerical accuracy. Moreover, the numerical accuracies of these two methods are highest from those of all methods given in tables 1, 2.

From figure 6(a) and table 2 it follows that, despite the closeness of the values of the mixing potential calculated within the inverse Monte Carlo and iteration methods for the first 24 coordination shells (see table 1), the corresponding Fourier transforms are found to have a noticeable difference in the vicinity of the centre of the first Brillouin zone (i.e. Γ point). The denoted difference is essentially decreased (see figure 6(a) and table 2) by putting the values of the mixing potential calculated within the iteration method for all coordination shells beginning with 25th one equal to zero (in analogy with the results of the inverse Monte Carlo simulations). The difference still remaining after such a procedure may be explained by the wide confidence intervals of the results of the inverse Monte Carlo method and/or by an effect of the boundary conditions on these results due to the insufficiently large size of simulation sample [28].

Table 2. The same as in table 1, but for the values of the Fourier transform of the mixing potential in the high-symmetry points [37] within the first Brillouin zone. The designation 'VM(24 shells)' corresponds to the accounting of the values of the mixing potential calculated in the framework of the variational method only for 24 coordination shells in a calculation of the Fourier transform.

	Γ	X	L	W
SM	0.237	−0.136	0.301	−0.309
ITM	0.353	−0.142	0.284	−0.329
VM	0.346	−0.146	0.289	−0.330
VM (24 shells)	0.291	−0.143	0.279	−0.324
IMC	0.212	−0.134	0.271	−0.328
TMG	0.367	−0.153	0.281	−0.335
CVM	0.590	−0.178	0.254	−0.328

7. Conclusions

In the present paper, in the framework of the high-accuracy ring approximation elaborated by the authors [14–17] in the context of the modified thermodynamic perturbation theory as applied to the lattice gas model, two methods are developed for calculation of the atomic interaction parameters in binary disordered alloys with Bravais crystal lattices on the basis of the information about atomic short-range order. One of them is the iteration method (section 4) resulting in explicit analytical relationships; the other one is the variational method (section 5).

The iteration method is simpler in application than the variational one. It was demonstrated (sections 4–6) that the iteration method has wide temperature–concentration

intervals of usability. This method may lead to essential error in calculations only in the case of alloy with short-range atomic interactions and/or with a small concentration of impurity, as well as in the case of an alloy whose temperature is close to the phase transition temperature. The variational method is comparatively more complicated in realization but permits us to achieve a high numerical accuracy of results in wider temperature–concentration intervals than the iteration one. However, a high convergence of the variational method with an increase of the number of variable parameters ensures the relative simplicity of calculations within this method as well. The numerical accuracies of the results of both methods are easy to control.

The important advantage of both iteration and variational methods is the use of the Fourier components of SRO parameters as initial data for calculations. Thus, the most complete experimental information on SRO in alloys may be taken into account, being especially important in the case of alloys with long-range atomic interactions and/or of alloys whose temperature is close to the phase transition temperature (due to corresponding increase of the effective radius of interatomic correlations). It should be noted that, for example, in the framework of the much used inverse Monte Carlo method, SRO in alloy can be described only by means of the values of SRO parameters for a number of coordination shells limited by an increase of the computational effort.

The other important advantage of both elaborated methods is the ability to calculate the interatomic interaction parameter for an *arbitrary* given coordination shell as well as the Fourier transform of the interatomic potentials. The information concerning the denoted Fourier transform may be useful, for example, for the estimation of the long-range contribution to atomic interactions in alloy caused by the relaxation of the elastic distortion fields induced by solute atoms [5, 25, 29–36]. Note that the much used inverse Monte Carlo and cluster variation methods allow us to calculate the values of the atomic interaction parameters only in real space, and the number of these parameters is significantly limited by an increase of the computational effort.

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