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# Anaytical methods for calculation of the short-range order in alloys: II. Numerical accuracy study

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**Abstract.** The numerical accuracy of the analytical approximations elaborated in part I and of a variety of other approximations advanced to date is examined, accepting the data on the short-range order parameters obtained by the Monte Carlo method as a standard. The approximations exhibiting the most promise for description of actual alloys and other lattice systems (for instance, interstitial alloys, semiconductors and magnetics) including those with a long-range character of atomic interactions are revealed. It is stated that, in the framework of the lattice gas model within a modified thermodynamic perturbation theory, the choice of the inverse effective number of atoms interacting with one fixed atom as a small parameter of the cumulant expansion along with taking account of the contributions from only linked irreducible diagrams ensures the fastest convergence of expansion. It is demonstrated that the use of the grand canonical ensemble yields the highest numerical accuracy in the statistical–thermodynamic description within the framework of all approximations elaborated in part I.

## 1. Introduction

In part I of the present work [1] (hereafter referred to as I), on the basis of the lattice gas model, in the framework of a number of approximations in a modified thermodynamic perturbation theory within the grand canonical ensemble, by the use of the thermodynamic fluctuation method, the expressions for the Fourier transform $\alpha_{\boldsymbol{k}}$ of the short-range order (SRO) Warren–Cowley parameters [2, 3] were obtained for the case of a two-component disordered alloy, whose $N$ sites form a Bravais crystal lattice. Those expressions are the following:

(1) in the zero approximation

$$\alpha_{\boldsymbol{k}} = [1 + \tilde{W}_{\boldsymbol{k}} c(1-c)/(k_{\mathrm{B}}T)]^{-1} \tag{1.1}$$

—the well known formula previously obtained within the spherical model [4–14] and below named the spherical model approximation;

(2) in the ring approximation (see also [15])

$$\alpha_{\boldsymbol{k}} = [I + \tilde{W}^{\mathrm{eff}}_{\boldsymbol{k}} c(1-c)/(k_{\mathrm{B}}T)]^{-1} \tag{1.2}$$

where

$$I = N^{-1} \sum_{\boldsymbol{q}} [1 + \tilde{W}_{\boldsymbol{q}} c(1-c)/(k_{\mathrm{B}}T)]^{-1}$$

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$$\tilde{W}_{\boldsymbol{k}}^{\mathrm{eff}} = \tilde{W}_{\boldsymbol{k}} - \frac{(1-2c)^2}{2k_{\mathrm{B}}T} N^{-1} \sum_{\boldsymbol{q}} \tilde{W}_{\boldsymbol{q}} \tilde{W}_{\boldsymbol{k}-\boldsymbol{q}} \left[1 + \frac{c(1-c)}{k_{\mathrm{B}}T} \tilde{W}_{\boldsymbol{q}}\right]^{-1} \left[1 + \frac{c(1-c)}{k_{\mathrm{B}}T} \tilde{W}_{\boldsymbol{k}-\boldsymbol{q}}\right]^{-1};$$

(3) in the high-temperature approximation of the $n$th order ($n = 0, 1, 2$)

$$\alpha_{\boldsymbol{k}} = \left[1 + \sum_{i=0}^{n} \tilde{W}_{\boldsymbol{k}}^{(i)} c(1-c)/(k_{\mathrm{B}}T)\right]^{-1} \tag{1.3}$$

where

$$\tilde{W}_{\boldsymbol{k}}^{(0)} = \tilde{V}_{\boldsymbol{k}}$$

$$\tilde{W}_{\boldsymbol{k}}^{(1)} = (k_{\mathrm{B}}T)^{-1} \left\{ c(1-c) N^{-1} \sum_{\boldsymbol{q}} (\tilde{W}_{\boldsymbol{q}})^2 - (1-2c)^2 \sum_{\boldsymbol{q}} \tilde{W}_{\boldsymbol{q}} \tilde{W}_{\boldsymbol{k}-\boldsymbol{q}}/2 \right\}$$

$$\tilde{W}_{\boldsymbol{k}}^{(2)} = (k_{\mathrm{B}}T)^{-2} \left\{ c(1-c)(1-2c)^2 \left[ N^{-1} \sum_{\boldsymbol{q}} (\tilde{W}_{\boldsymbol{q}})^2 \tilde{W}_{\boldsymbol{k}-\boldsymbol{q}} - N^{-2} \sum_{\boldsymbol{q}_1, \boldsymbol{q}_2} \tilde{W}_{\boldsymbol{q}_1} \tilde{W}_{\boldsymbol{q}_2} \tilde{W}_{\boldsymbol{q}_1+\boldsymbol{q}_2} \right] \right.$$
$$\left. + [1-6c(1-c)]^2 N^{-2} \sum_{\boldsymbol{q}_1, \boldsymbol{q}_2} \tilde{W}_{\boldsymbol{q}_1} \tilde{W}_{\boldsymbol{q}_2} \tilde{W}_{\boldsymbol{k}-\boldsymbol{q}_1-\boldsymbol{q}_2}/6 - [c(1-c)]^2 N^{-1} \sum_{\boldsymbol{q}} (\tilde{W}_{\boldsymbol{q}})^3 \right\};$$

(4) in the chain approximation

$$\alpha_{\boldsymbol{k}} = [1 + \tilde{W}_{\boldsymbol{k}}^{\mathrm{eff}} c(1-c)/(k_{\mathrm{B}}T)]^{-1} \tag{1.4}$$

where

$$\tilde{W}_{\boldsymbol{k}}^{\mathrm{eff}} = \frac{\tilde{W}_{\boldsymbol{k}} + c^2[(\tilde{W}_{\boldsymbol{k}=0})^2 + \tilde{W}_{\boldsymbol{k}} \tilde{W}_{\boldsymbol{k}=0}(2 + c\tilde{W}_{\boldsymbol{k}=0}/(k_{\mathrm{B}}T))]/(k_{\mathrm{B}}T)}{[1 + \tilde{W}_{\boldsymbol{k}=0} c(1-c)/(k_{\mathrm{B}}T)]^2 [1 + \tilde{W}_{\boldsymbol{k}} c(1-c)/(k_{\mathrm{B}}T)]};$$

(5) in the low-concentration approximation

$$\alpha_{\boldsymbol{k}} = \{1 + c(1-c)[1 - \exp(-\mu/(k_{\mathrm{B}}T)) - \mu/(k_{\mathrm{B}}T) + \tilde{f}_{\boldsymbol{k}}]\}^{-1} \tag{1.5}$$

where

$$\tilde{f}_{\boldsymbol{k}} = \sum_{\boldsymbol{R}} [1 - \exp(-V_{\boldsymbol{R}}/(k_{\mathrm{B}}T)) \exp(-\mathrm{i}\boldsymbol{k} \cdot \boldsymbol{R}).$$

In all expressions, the function $\tilde{W}_{\boldsymbol{k}}$ is determined as

$$\tilde{W}_{\boldsymbol{k}} = \tilde{V}_{\boldsymbol{k}} + \mu \tag{1.6}$$

where $\tilde{V}_{\boldsymbol{k}}$ is the Fourier transform of the (pair) mixing potential and $\mu$ is the quantity to be found from the equation of the following form common for all approximations

$$N^{-1} \sum_{\boldsymbol{q}} \alpha_{\boldsymbol{q}} = 1 \tag{1.7}$$

on substitution of the function $\alpha_{\boldsymbol{k}}$ corresponding to each approximation. The summations on the wave vectors $\boldsymbol{q}$ and $\boldsymbol{q}_i$ are carried over all points in the first Brillouin zone specified by the cyclic boundary conditions, $T$ is the absolute temperature, $k_{\mathrm{B}}$ is the Boltzmann constant and $c$ is the concentration.

Notice that, being written down within the framework of the canonical ensemble (i.e. at $\mu = 0$, see I), the expressions for the SRO parameters obtained within the high-temperature approximation of the third order and the low-concentration approximation are identical to the expressions obtained by Semenovskaya [16] and by Krivoglaz [17–19], respectively. That is why, below, we shall call these approximations the modified Semenovskaya and modified Krivoglaz low-concentration approximations, respectively.

The purpose of the present work is to analyse the relative numerical accuracy as well as the temperature–concentration and effective radius of atomic interaction intervals of

quantitative adequacy of the above-mentioned approximations and of a number of other ones† (including those obtained within the framework of the canonical ensemble) on the basis of the comparison of their results with those of the Monte Carlo simulations (see also section 12 in I).

In section 2, the procedure of the Monte Carlo simulations used in the present investigations is described. In section 3, the comparative study of the numerical accuracy of the results obtained by the use of the canonical and grand canonical ensembles as well as by the use of two types of normalization of the correlation function (by summands and by a multiplier) is performed within a number of approximations. In section 4, the problem of the choice of the physically adequate solution of the nonlinear integral equation (1.7) is discussed. In section 5, the relative numerical accuracy and the intervals of correct applicability of the approximations elaborated in I and of a number of others are analysed. In section 6, the obtained results are summarized.

## 2. Procedure of the Monte Carlo simulations

In the present work, the standard Monte Carlo method within the canonical ensemble under the periodical boundary conditions [20] was applied. At every given temperature, the equilibrium configuration obtained for the closest, higher temperature from the set of already investigated ones (or the random distribution for the highest temperature) was used as an initial configuration for the subsequent transition into an equilibrium state. The absence of a monotonic change of mean values of each quantity being calculated at Monte Carlo simulations was chosen as a criterion for the achievement of an equilibrium state. To fulfil such a criterion, it was generally required to perform 1000–20 000 Monte Carlo (MC) steps (i.e. the interchanges of two accidentally chosen atoms) per site.

After the achievement of an equilibrium state, at every subsequent MC step the averaging of each calculated quantity was performed over all MC steps carried out at an equilibrium state. When the oscillation amplitudes of such averages (being considered as a function of the number of the performed MC steps) became less than 5% (of the absolute value of the corresponding average) during the last 10% of steps (from the total number of steps carried out at an equilibrium state), the values of the averages calculated at the last MC step were accepted as equilibrium ones.

At every temperature, to eliminate the effect of the boundary conditions, the simulations were consequently performed at increasing numbers of sites in a sample $N = 20^3, 30^3, 40^3, \ldots$, until the difference between the simulation results at the last and penultimate steps became less than 5% (of the absolute value of these results). Then, the results obtained at the last step were accepted as the desired results of simulations at the corresponding given temperature.

## 3. Statistical ensemble choice

All the expressions for $\alpha_k$ obtained in I by the use of the grand canonical ensemble can be initially written in the following common form

$$\alpha_k = 1 - N^{-1} \sum_q \beta_q + \beta_k \tag{3.1}$$

† The consideration of the approximations additional to those obtained in I is dictated by the absence in the literature of a comparative review of a variety of approximations advanced to date.

where $\beta_k$ is a functional of $\tilde{W}_k = \tilde{V}_k + \mu$ specified for each approximation. In I, from the general thermodynamic relationships for the grand canonical ensemble, it is stated that the quantity $\mu$ entering (3.1) through the function $W_k$ must satisfy the equation

$$N^{-1} \sum_q \beta_q = 1. \tag{3.2}$$

Substitution of (3.2) into (3.1) gives

$$\alpha_k = \beta_k. \tag{3.3}$$

Notice that, in section 1, the expressions for all approximations are written just in the form (3.3).

From the general expression for the grand partition function, it follows (see section 2 in I) that, in (3.1), the transition in consideration from the grand canonical ensemble to the canonical one may be formally realized by setting $\mu = 0$ or, equivalently, by the substitution of $\tilde{V}_k$ instead of $\tilde{W}_k$. After such a transition, in general, the equality (3.2) will not be satisfied, and, therefore, within the framework of the canonical ensemble, the expression (3.3) turns out to be invalid, and the initial expression (3.1) with $\mu = 0$ should be used for the calculations of $\alpha_k$.

It is obvious that, owing to the presence of the normalizing summands complementary to $\beta_k$ in (3.1), the function $\alpha_k$ determined by (3.1) satisfies the constraint [7, 21–25]

$$N^{-1} \sum_q \alpha_q = 1 \tag{3.4}$$

for an arbitrary form of the function $\beta_k$, in particular, independently of the type of statistical ensemble used for derivation of this function. Let us call such a way of satisfaction of the constraint (3.4) as in (3.1) normalization by summands. Another normalization method was established by Clapp and Moss [21, 22]. It lies in the introduction of a normalizing multiplier and results in the following expression, alternative to (3.1)

$$\alpha_k = \beta_k \left[ N^{-1} \sum_q \beta_q \right]^{-1}. \tag{3.5}$$

Let us call such a way of satisfaction of the constraint (3.4) as in (3.5) normalization by multiplier.

We performed the comparative analysis of the numerical accuracy of the expression (3.1) written down within the framework of both canonical and grand canonical ensembles, as well as the accuracy of the expression (3.5) (within the canonical ensemble) for all approximations listed in section 1. The cases $c = 0.01$, 0.1, 0.25 and 0.5 for f.c.c. alloy with two types of mixing potential that correspond to taking account of one ($V_1 > 0$) and two ($V_1 > 0$, $V_2 = -0.5V_1$) shells of atomic interactions ($V_s$ is the mixing potential for the $s$th coordination shell) were considered. The calculations were performed for the temperature interval $[T_0, 2T_0]$, where $T_0$ is the temperature of the corresponding order–disorder phase transition. The conclusions on the relative accuracy of approximations were done on the basis of the comparison of the corresponding values of the SRO parameters for the first four coordination shells with those obtained by the Monte Carlo method.

It was revealed that, within the framework of the spherical model (1.1), ring (1.2), modified Semenovskaya (1.3) and chain (1.4) approximations, the application of the grand canonical ensemble ensures the highest numerical accuracy in all considered cases (see e.g. figures 1 and 2). For all these approximations, the advantage in accuracy caused by the use of the grand canonical ensemble essentially increases when the concentration approaches the equiatomic value. So, for instance, within the ring approximation, such

a tendency is demonstrated in figure 2. The use of normalization by multiplier (3.5) instead of normalization by summands within the canonical ensemble results in considerably less rise of the numerical accuracy of approximations than the use of the grand canonical ensemble (see e.g. figures 1 and 2). The results obtained within the framework of all four approximations by the use of the canonical ensemble (with normalization both by summands and by multiplier) are characterized by an overvalued critical temperature of order–disorder phase transition (determined by the singularity in the temperature dependence of the SRO parameters), which, in a number of cases (see e.g. figures 2(c), (d)), may be twice as much as the temperature of the phase transition calculated by the Monte Carlo method. Note that the spherical model approximation written down within the framework of the canonical ensemble without any normalization and within the canonical ensemble with multiplier normalization is identical to the well known Krivoglaz [18, 19, 26] and Krivoglaz–Clapp–Moss [21, 22] approximations, respectively.

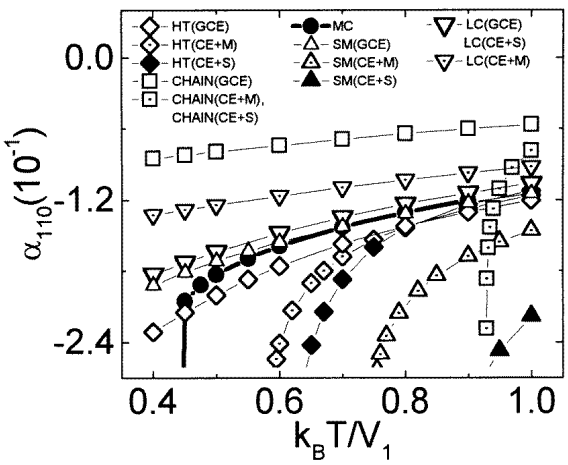


**Figure 1.** The dependencies of the SRO parameters for the first coordination shell of the f.c.c. crystal lattice on the reduced temperature obtained by the Monte Carlo simulations (MC) and within the framework of the spherical model (1.1) (SM), modified Semenovskaya (1.3) (HT), chain (1.4) (CHAIN) and Krivoglaz low-concentration (1.5) (LC) approximations with the use of the grand canonical ensemble (GCE) and of the canonical ensemble with normalization by multiplier (3.5) (CE + M) and by summands (3.1) (CE + S) for every approximation at $c = 0.25$, $V_1 > 0$, $V_s = 0$ ($s > 1$).

In all considered cases, within the framework of the modified low-concentration Krivoglaz approximation, the applications of both the canonical ensemble with normalization by summands and the grand canonical ensemble lead to the same results, because, in all considered cases, the approximate solution $\mu = 0$ turns out to be the physically adequate solution of the equation (1.7) (or, respectively, (3.2)) within the framework of this approximation (for more details, see the next section). Note that the use of the canonical ensemble with the multiplier normalization results in the *decrease* of the numerical accuracy of the modified low-concentration Krivoglaz approximation in a number of cases (see e.g. figure 1).

Thus, on the basis of the performed analysis, one may conclude that, to obtain the results of the highest numerical accuracy, the grand canonical ensemble should be used in the statistical–thermodynamic description within the framework of all approximations listed in section 1. Only in the case of relatively low concentrations (for the modified

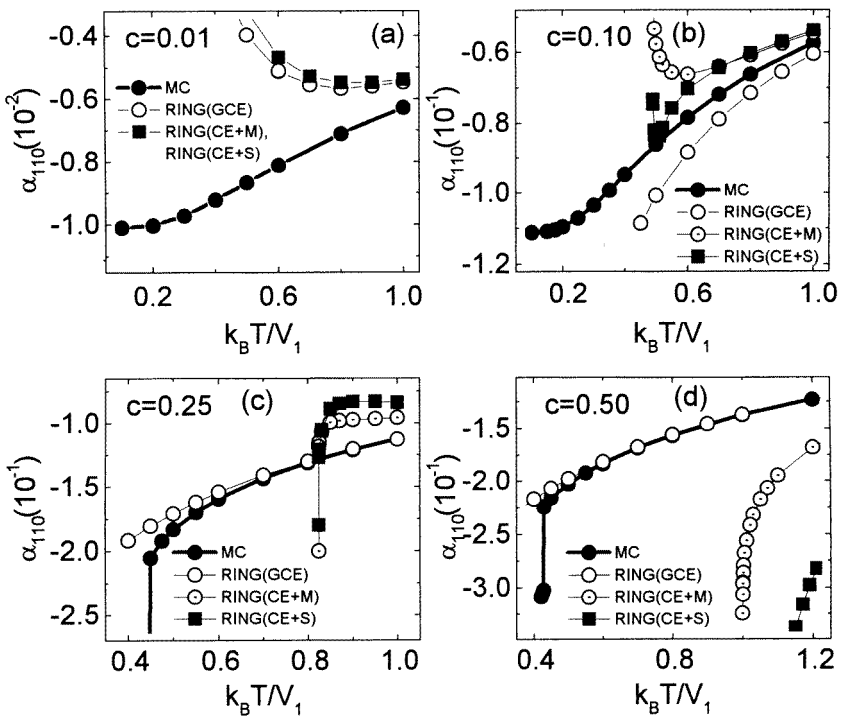


**Figure 2.** The dependencies of the SRO parameters for the first coordination shell of the f.c.c. crystal lattice on the reduced temperature obtained by the Monte Carlo simulations (MC) and within the framework of the ring (1.2) (RING) approximation with the use of the grand canonical ensemble (GCE) and of the canonical ensemble with normalization by multiplier (3.5) (CE + M) and by summands (3.1) (CE + S) at $V_1 > 0$, $V_s = 0$ ($s > 1$) and (a) $c = 0.01$, (b) $c = 0.1$, (c) $c = 0.25$ and (d) $c = 0.5$.

low-concentration Krivoglaz approximation—at any concentration), may one restrict consideration to the canonical ensemble, because in this case the results weakly depend (or do not depend at all) on the type of statistical ensemble being used. Thus, in section 5, at the analysis of the relative numerical accuracy of approximations, those listed in section 1 will be included in consideration within only the grand canonical ensemble.

In conclusion of this section, it must be emphasized that the inverse transition in consideration from the canonical ensemble to the grand canonical one may *not* be formally realized by the substitution of $\tilde{W}_{\boldsymbol{k}} = \tilde{V}_{\boldsymbol{k}} + \mu$ instead of $\tilde{V}_{\boldsymbol{k}}$ in the general case. This is evident, for example, from the high-temperature approximation (1.3), in which such substitution would result in $\tilde{W}_{\boldsymbol{k}}^{(0)} \to \tilde{V}_{\boldsymbol{k}} + \mu$, whereas in both statistical ensembles we have $\tilde{W}_{\boldsymbol{k}}^{(0)} = \tilde{V}_{\boldsymbol{k}}$. Furthermore, such substitution may be incorrect for approximations elaborated without the formalism of paper I. For example, this is the case of the Tahir-Kheli approximation [27], in which the grand canonical ensemble was *initially* used in the consideration, although a quantity like $\mu$ does not enter the corresponding finished expressions. Besides, our numerical test revealed that the numerical accuracy of the Tahir-Kheli approximation modified by the substitution of $\tilde{V}_{\boldsymbol{k}} + \mu$ instead of $V_{\boldsymbol{k}}$ may be less than that of the unmodified one in a number of cases.

## 4. Solution of the equation (1.7)

As a rule, solving the nonlinear equation (1.7) (or, respectively, (3.2) for the quantity $\mu$ within the framework of the approximations listed in section 1, one arrives at the problem of a choice of physically adequate solution. Within the spherical model, chain and modified low-concentration Krivoglaz approximations, in all considered cases, this problem was resolved by means of the choice of a solution of the equation (1.7) that meets the following inequality under given temperature and concentration and arbitrary values of the wave vector

$$\alpha_{\boldsymbol{k}}(T, c, \mu) > 0 \tag{4.1}$$

which is the necessary condition of stability (or metastability) of the disordered state of the alloy [28]. Notice that the boundary of the interval of the values of $\mu$ that satisfy the condition (4.1) is characterized by a singular behaviour of the quantity $\alpha_{\boldsymbol{R}=\mathbf{o}} = N^{-1}\sum_{\boldsymbol{q}}\alpha_{\boldsymbol{q}}$ as a function of $\mu$, due to the vanishing (under the change of sign) of the quantity $\alpha_{\boldsymbol{k}}^{-1}$ for the definite wave vectors at a value of $\mu$ corresponding to the boundary. This fact provides the possibility of graphical estimation of the region of the values of $\mu$ that meet the condition (4.1), by means of plotting the dependence of the quantity $\alpha_{\boldsymbol{R}=\mathbf{o}}$ on $\mu$.

In the framework of the ring and modified Semenovskaya approximations, even within the region of the values of $\mu$ that meet the condition (4.1), it was found that there exist, as a rule, a few solutions of the nonlinear equation (1.7). For these two approximations, the problem of choice of the physically adequate solution was resolved by a consideration of the case of the extremely high temperatures, when the results of any statistical–thermodynamic approximation asymptotically approach the corresponding exact results, owing to the vanishing of the interatomic correlations. In particular, in such a limiting case, the results obtained within the framework of the canonical and grand canonical ensembles must asymptotically approach each other, due to the equivalence of these ensembles in the case of exact consideration (see e.g. [29]). Because, within the framework of formalism developed in I, the transition from the grand canonical ensemble to canonical one corresponds to the appropriation of the zero value to $\mu$, it follows that only the solution of the equation (1.7) that asymptotically tends to zero at $T \to \infty$ under any value of concentration is physically adequate.

In all considered cases, we revealed that under a given type of mixing potential there always exists a *unique* solution of the equation (1.7) that satisfies the denoted criterion, and just this distinguished solution ensures the highest numerical accuracy of the results of the calculations of the SRO parameters. So, for example, in the case $c = 0.25$, $k_{\mathrm{B}}T/V_1 = 1.8$, $V_1 > 0$, $V_2 = -0.5V_1$, $V_s = 0$ ($s > 2$) the dependence of the quantity $\alpha_{\boldsymbol{R}=\mathbf{o}} = N^{-1}\sum_{\boldsymbol{q}}\alpha_{\boldsymbol{q}}$ on $\mu$ within the framework of the ring approximation (1.2) is as shown in figure 3(a). In the region of the values of $\mu$ that meets the condition (4.1) ($\mu > \mu_c$ in figure 3(a)–(c)), there are three solutions of equation (1.7) numbered by 1, 2, 3 in figure 3. However, only one of these solutions (number 2 in figure 3(a)–(c)) satisfies the condition of the asymptotical vanishing at $T \to \infty$ for *both* $c = 0.1$ and $c = 0.25$ (see figure 3(b), (c)). The highest numerical accuracy of the results on the SRO parameters corresponding to physically adequate solution number 2 is demonstrated in figure 3(d), (f).

It should be noted that within the framework of the ring and modified Semenovskaya approximations, there exist the temperature–concentration intervals in which the physically adequate solution of the equation (1.7) becomes approximate rather than exact. For instance, in the previous case, at $k_{\mathrm{B}}T/V_1 < 1.5$, the solutions number 1 and 2 merge together and satisfy the equation (1.7) only approximately (see figure 3(e)). Nevertheless, for calculations of the SRO parameters, one should use just this approximate solution, because it meets

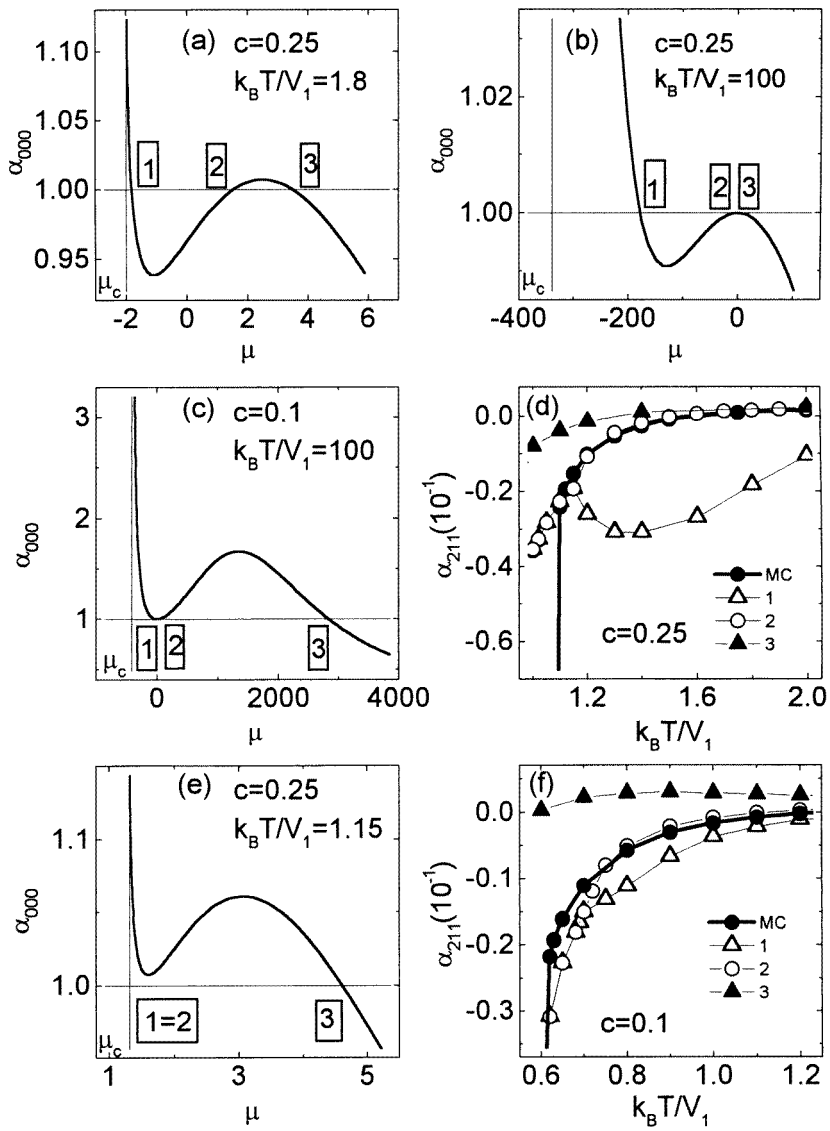


**Figure 3.** The dependencies of the quantity $\alpha_{000} = \alpha_{R=o} = N^{-1}\sum_q \alpha_q$ on $\mu$ at (a) $c = 0.25$, $k_BT/V_1 = 1.8$; (b) $c = 0.25$, $k_BT/V_1 = 100$; (c) $c = 0.1$, $k_BT/V_1 = 100$; (e) $c = 0.25$, $k_BT/V_1 = 1.15$ and the dependencies of the SRO parameter $\alpha_{211}$ corresponding to different solutions of the equation (1.7) on the reduced temperature $k_BT/V_1$ at (d) $c = 0.25$ and (f) $c = 0.1$ obtained within the framework of the ring (1.2) approximation in the case of $V_1 > 0$, $V_2 = -0.5V_1$, $V_s = 0$ ($s > 2$).

the condition $\mu \to 0$ at $T \to \infty$ for every concentration, despite the existence of the other, exact solution (number 3 in figure 3(e)), which does not meet this condition. In all considered cases, the validity of the above statement is confirmed under the comparison of the numerical accuracy of the calculations of the SRO parameters by the use of physically adequate, approximate and inadequate, exact solutions (see e.g. the region $k_BT/V_1 < 1.5$

in figure 3(d)). It is notable that, using the approximate solution of the equation (1.7) in calculations of the SRO parameters, one should apply the expression (3.1) rather than (3.3) even in the case of the grand canonical ensemble.

## 5. Numerical accuracy of approximations

In figures 4–11, the dependencies of the SRO parameters for the first four coordination shells of the f.c.c. crystal lattice on the reduced temperature $k_B T/V_1$, which we obtained by the Monte Carlo simulations (see section 2) as well as within a number of analytical approximations, are plotted. The data corresponding to the disordered state of alloy obtained by Golosov *et al* [30, 31] within the framework of the cluster-variation method in the tetrahedral approximation are also presented. For each of the concentrations $c = 0.01$, 0.1, 0.25 and 0.5†, two following types of mixing potential: $V_1 > 0$, $V_s = 0$ ($s > 1$) and $V_1 > 0$, $V_2 = -0.5V_1$, $V_s = 0$ ($s > 2$) are used. Such a choice permits us to reveal the tendencies in the change of the numerical accuracy of approximations under a variation of both the concentration and effective radius of atomic interactions. In each case, the $[T_0, 2T_0]$ temperature interval is considered ($T_0$ is the temperature of the order–disorder phase transition), because such an interval is the most important in view of the experimental measurements of the SRO parameters. In figures, the point of the phase transition corresponds to the abrupt change or to the point of inflection of the temperature dependence of the SRO parameters obtained by the Monte Carlo method‡.

In the case of approximate coincidence of curves corresponding to different approximations, with the aim of clarity, the unique curve is plotted and put in correspondence to all such approximations. The absence of a curve corresponding to some approximation in a figure indicates that, owing to the low numerical accuracy of this approximation, a corresponding curve cannot be presented within the considered temperature interval (i.e. $T_c > 2T_0$) and/or the inclusion of this curve in the figure results in visual indistinguishability of the other curves. For example, this is the case of $c = 0.5$, $V_2 = 0$, when the value of the reduced temperature $k_B T/V_1 = 1$ is critical for the Krivoglaz–Clapp–Moss [18, 19, 21, 22, 26] approximation, whereas the corresponding value of the reduced temperature of the phase transition obtained by the Monte Carlo method $k_B T/V_1 = 0.44$, and, therefore, the results obtained within this approximation cannot be presented in the considered $[T_0, 2T_0]$ temperature interval in the corresponding figure 10.

Accepting the results of the Monte Carlo method as a standard, on the basis of the data presented in figures 4–11, one may conclude the following.

In all considered cases, except for relatively low concentrations $c = 0.01$ ($V_2 = 0$ and $V_2 \neq 0$), $c = 0.1$ ($V_2 = 0$), the ring (1.2) approximation yields adequate§ results in the entire temperature interval excluding the immediate vicinity of the phase transition temperature. Note that, in the cases $c = 0.25$, $V_2 \neq 0$ (figure 9) and $c = 0.5$, $V_2 \neq 0$ (figure 11), the ring approximation is adequate even at the temperature of the phase transition. The numerical accuracy of this approximation essentially rises when the concentration approaches the

† The consideration of concentrations greater than the equiatomic one is not required due to the invariance of statistical–thermodynamic properties of the alloys with concentration-independent pair atomic interactions with respect to the transformation $c \to (1 - c)$ [32].

‡ It should be noted that the lowest temperature limit of applicability of all the considered approximations is the *critical* temperature $T_c$ of the absolute instability of the disordered state rather than the temperature $T_0$ of the order–disorder phase transition ($T_c \leqslant T_0$). Thus, it is obvious that the SRO shown in figures 1–11 for a number of approximations at $T < T_0$ is metastable.

§ Below, unless otherwise specified, the term 'adequacy of an approximation' is used in reference to the high numerical accuracy of an approximation for the coordination shells from first to fourth, inclusive.

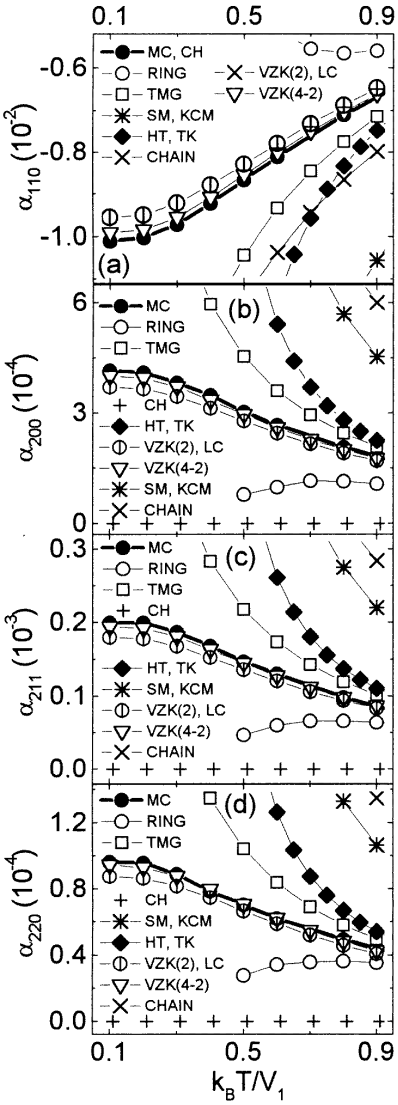


**Figure 4.** The dependencies of the SRO parameters for the (a) first, (b) second, (c) third and (d) fourth coordination shells of the f.c.c. crystal lattice on the reduced temperature obtained within the framework of the Monte Carlo method (MC), Krivoglaz–Clapp–Moss formula [18, 19, 21, 22, 26] (KCM) as well as the spherical model (1.1) (SM), ring (1.2) (RING), modified Semenovskaya (1.3) (HT) and Krivoglaz low-concentration (1.5) (LC), chain (1.4) (CHAIN), Tokar–Masanskii–Grishchenko [12, 34] (TMG), Christy–Hall [35] (CH), Vaks–Zein–Kamyshenko two-cluster (VZK(2)) and 4–2-cluster (VZK(4–2)) [33] and Tahir-Kheli [27] (TK) approximations at $c = 0.01$, $V_1 > 0$, $V_s = 0$ ($s > 1$).

equiatomic value and/or when the atomic interactions on the second coordination shell are taken into account. Notice that the latter fact is in accordance with the choice of the inverse effective number of atoms interacting with one fixed atom as a small parameter in the corresponding perturbation theory within the ring approximation. The high numerical accuracy of this approximation even in the cases of the short-range atomic interactions

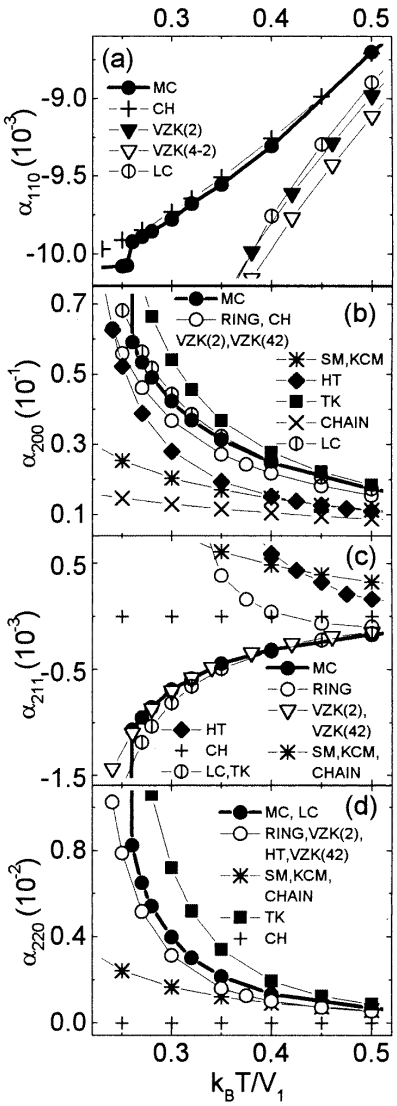


**Figure 5.** The same as in figure 4 at $c = 0.01$, $V_1 > 0$, $V_2 = -0.5V_1$, $V_s = 0$ ($s > 2$).

clearly demonstrates the quick convergence of the cumulant expansion under such a choice of small parameter.

The spherical model (1.1) and modified Semenovskaya (1.3) approximations yield adequate results at $c = 0.25$ and $c = 0.5$ for both used types of mixing potential, at all considered temperatures except for the immediate vicinity of the phase transition temperature. The Tahir-Kheli approximation [27] gives adequate results in a comparatively wide temperature interval only in two cases, $c = 0.25$, 0.5 at $V_2 \neq 0$. The numerical accuracy of the spherical model, modified Semenovskaya and Tahir-Kheli approximations rises as the atomic interactions at the second coordination shell are taken into account.

The Krivoglaz–Clapp–Moss formula [18, 19, 21, 22, 26] and the chain (1.4) approxima-

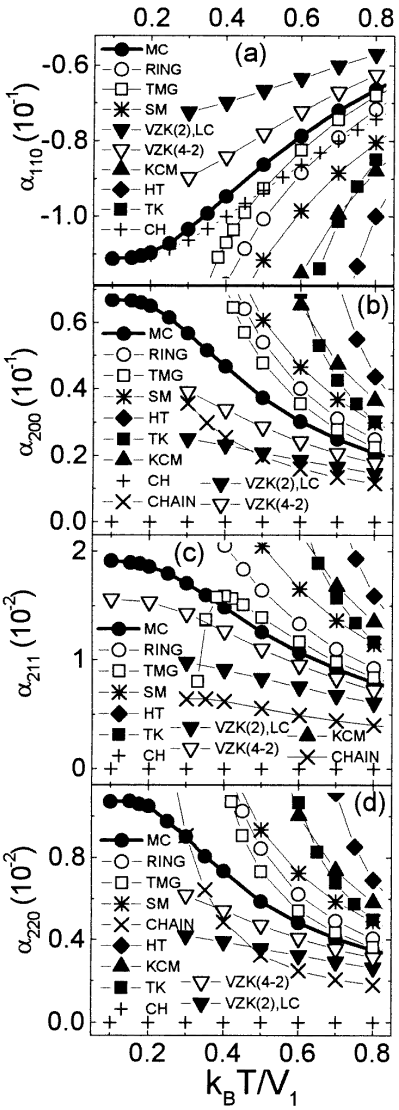


**Figure 6.** The same as in figure 4 at $c = 0.1$, $V_1 > 0$, $V_s = 0$ ($s > 1$).

tion yield adequate results in none of the considered cases, almost in the entire considered temperature interval. The numerical accuracy of the Krivoglaz–Clapp–Moss formula has a tendency to increase when the characteristic radius of atomic interactions enlarges as well as on decrease of concentration. The modified Krivoglaz low-concentration approximation yields adequate results in a wide temperature interval only in the cases $c = 0.01$, 0.25 at $V_2 = 0$, $c = 0.1$ at $V_2 \neq 0$. If $c \to 0$ the Krivoglaz low-concentration and both considered Vaks–Zein–Kamyshenko approximations [33] asymptotically approach each other. Note that the latter statement may be also easily proved analytically.

In the entire temperature interval except for the immediate vicinity of the phase transition temperature, the results obtained within the framework of the Tokar–Masanskii–Grishchenko approximation [12, 34] are adequate in all considered cases except for $c = 0.01$, $V_2 = 0$

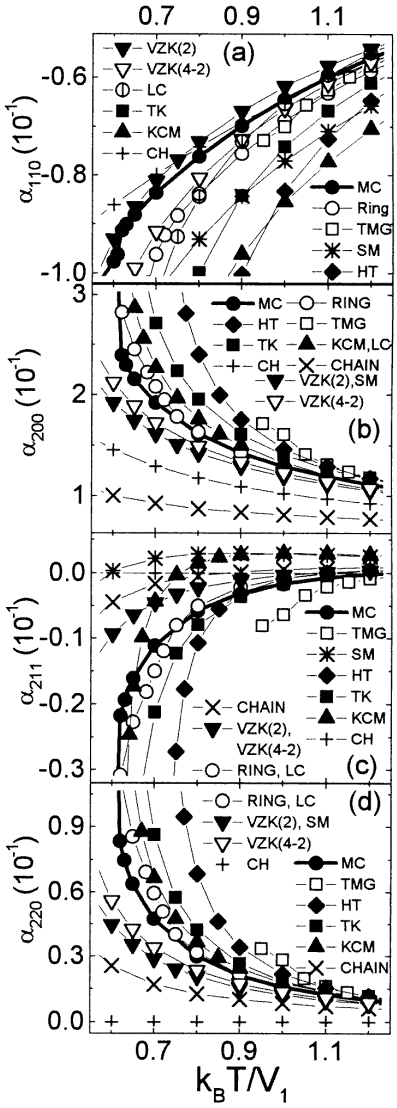


**Figure 7.** The same as in figure 4 at $c = 0.1$, $V_1 > 0$, $V_2 = -0.5V_1$, $V_s = 0$ ($s > 2$).

and $V_2 \neq 0$, $c = 0.1$, $V_2 \neq 0$. Note that, in two cases, $c = 0.01$, $V_2 \neq 0$ (for the entire considered temperature interval) and $c = 0.1$, $V_2 \neq 0$ (for reduced temperatures less than 0.91), the solutions of the corresponding set of nonlinear equations for determination of the SRO parameters within the framework of this approximation do not exist and thus cannot be presented in the corresponding figures 5 and 7.

The Vaks–Zein–Kamyshenko two-cluster approximation within the cluster-field method [33] gives adequate results in almost the entire considered temperature interval in the cases $c = 0.01$, $V_2 = 0$ and $c = 0.1$, 0.25, 0.5, $V_2 \neq 0$. For the Vaks–Zein–Kamyshenko 4–2-cluster approximation such cases are $c = 0.01$, $V_2 = 0$ and $c = 0.1$, 0.25, $V_2 = 0$ and $V_2 \neq 0$. The transition from the Vaks–Zein–Kamyshenko two-cluster approximation to the

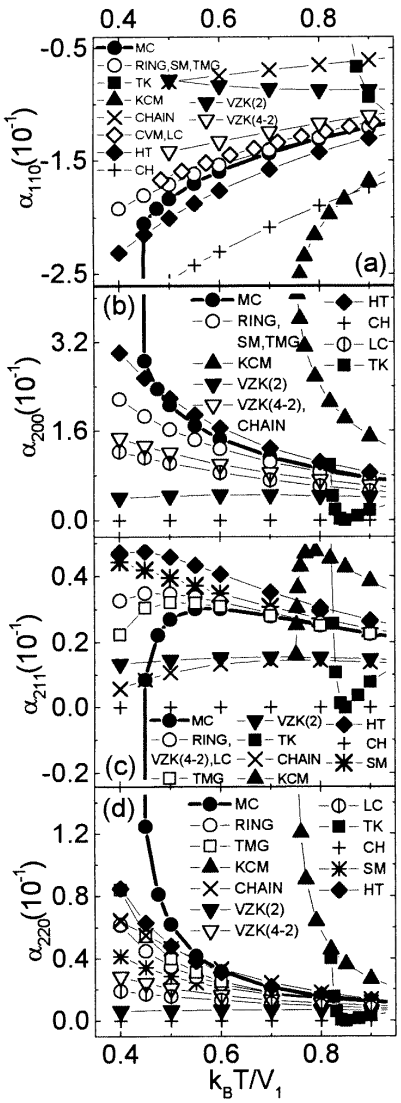


**Figure 8.** The same as in figure 4 at $c = 0.25$, $V_1 > 0$, $V_s = 0$ ($s > 1$). The CVM designation corresponds to the results of the cluster-variation method in the tetrahedral approximation from [30, 31].

4–2-cluster one leads to higher numerical accuracy of results in all considered cases, except for $c = 0.01$, 0.5, $V_2 \neq 0$. Thus, one can suppose that the convergence of the corresponding cluster expansion is not necessarily quick.

Within the Christy–Hall [35] approximation, the data on the SRO parameter for the first coordination shell are adequate in the cases $c = 0.01$, 0.1, $V_2 = 0$, $c = 0.1$, $V_2 \neq 0$, and for the second coordination shell in the case $c = 0.01$, $V_2 \neq 0$ for the whole considered temperature interval. It should be emphasized that, within the Christy–Hall approximation, the SRO parameters are identically equal to zero for all coordination shells with zero values of the mixing potential. Notice, also, that, taking into account the atomic interactions only

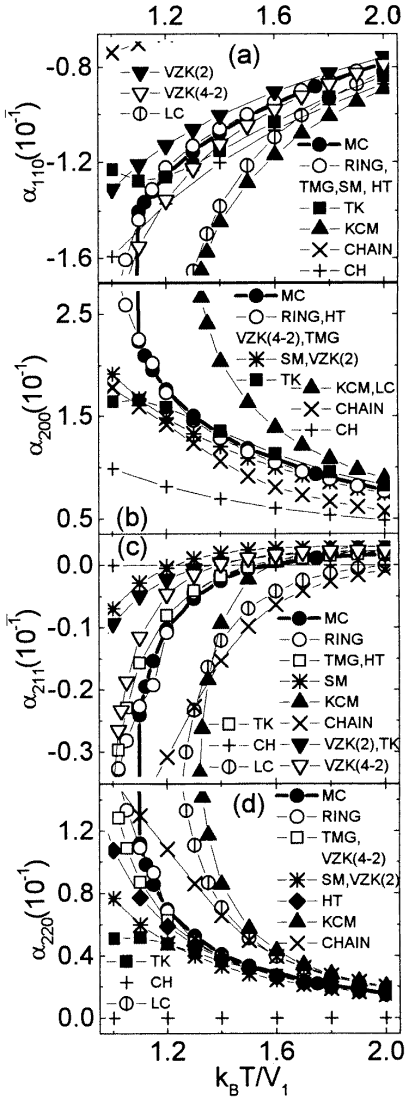


**Figure 9.** The same as in figure 4 at $c = 0.25$, $V_1 > 0$, $V_2 = -0.5V_1$, $V_s = 0$ ($s > 2$).

for the first coordination shell, this approximation yields the same results as within the quasichemical approximation for the SRO parameter for the first coordination shell (see e.g. [18, 36–38]).

The cluster-variation method in the tetrahedral approximation [30, 31] gives adequate results for the SRO parameter for the first coordination shell at $c = 0.25$, $V_2 = 0$ and adequate but somewhat less accurate ones at $c = 0.5$, $V_2 = 0$. However, in both cases, this method is at a disadvantage on the numerical accuracy in relation to the ring, spherical model and Tokar–Masanskii–Grishchenko approximations. Unfortunately, although, up to now, the cluster-variation method (in different modifications) has been extensively advanced (see e.g. [25, 30, 31, 39–46]), we could not carry out more detailed analysis of the numerical accuracy of this method, due to the absence of the appropriate numerical data in the literature.

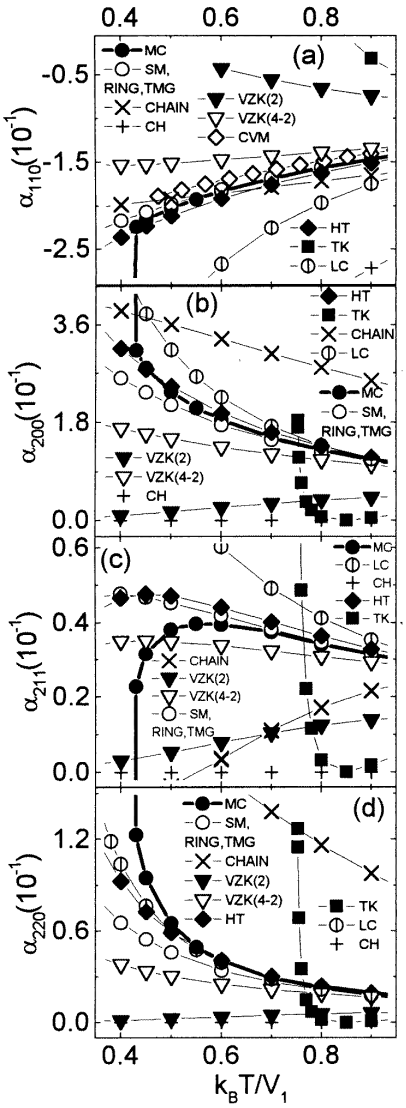


**Figure 10.** The same as in figure 8 at $c = 0.5$, $V_1 > 0$, $V_s = 0$ ($s > 1$).

In all above considered model cases, the short-range character of atomic interactions was imposed, in contrast to the case of actual alloys (see section 1 in I). That is why we considered the case of the $Ni_{0.89}Cr_{0.11}$ alloy at $T = 833$ K, for which detailed information on the atomic interactions as well as data on the Monte Carlo simulations were obtained by Schweika and Haubold [47]. In table 1, the results of the Monte Carlo simulations of the SRO parameters for the first 24 coordination shells in this alloy, as well as of the corresponding calculations carried out by us within the framework of the above discussed approximations, are summarized.

On the basis of the data presented in table 1, one can conclude that, in the case of the $Ni_{0.89}Cr_{0.11}$ alloy, the ring, Tokar–Masanskii–Grishchenko and Vaks–Zein–Kamyshenko 4–2-cluster approximations give the values of the SRO parameters that belong

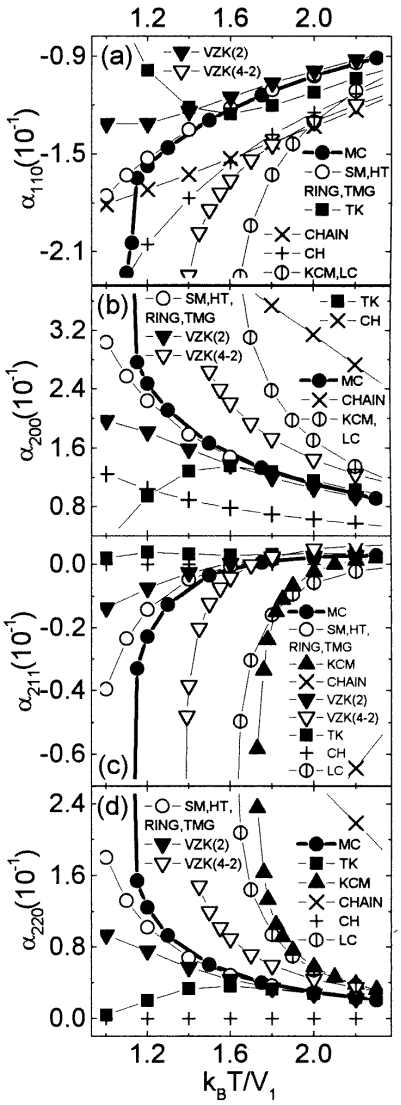


**Figure 11.** The same as in figure 4 at $c = 0.5$, $V_1 > 0$, $V_2 = -0.5V_1$, $V_s = 0$ ($s > 2$).

to the appropriate confidence intervals of the Monte Carlo method for all 24 considered coordination shells. The values obtained within the framework of the modified Krivoglaz low-concentration approximation do not belong to the appropriate confidence intervals of the Monte Carlo method for one (first), those within the Vaks–Zein–Kamyshenko two-cluster approximation for two (first, second), those within the spherical model approximation for three (first, third, fifth), and those within the modified Semenovskaya and Tahir-Kheli approximations for three (first, second, fifth) coordination shells, respectively. The Krivoglaz–Clapp–Moss formula as well as the chain and Christy–Hall approximations yield results that do not belong to the appropriate confidence intervals of the Monte Carlo method for six, eight and twelve coordination shells, respectively.

**Table 1.** The SRO parameters $\alpha_{lmn} \times 10^4$ (where $lmn$ is the index of the coordination shell) for $Ni_{0.89}Cr_{0.11}$ at $T = 833$ K. The designations of approximations are the same as in figures 4–11.

| *lmn* | MC[a] | Ring | TMG | SM | HT | TK | KCM | Chain | LC | CH | VZK(2) | VZK(42) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 110 | −536(18) | −555.4 | −540.8 | −614.8[b] | −591.6[b] | −569.8[b] | −653.6[b] | −341.1[b] | −514.0[b] | −564.6[b] | −513.7[b] | −537.8 |
| 200 | 391(20) | 390.4 | 396.9 | 386.9 | 425.1[b] | 419.9[b] | 419.8[b] | 247.4[b] | 408.2 | 312.3[b] | 368.0[b] | 378.9 |
| 211 | 93(10) | 97.8 | 94.8 | 111.0[b] | 104.7 | 97.9 | 123.2[b] | 83.4 | 89.3 | 44.2[b] | 88.5 | 93.0 |
| 220 | −115(10) | −114.0 | −116.1 | −118.0 | −116.4 | −115.3 | −126.0 | −69.3[b] | −118.3 | −133.2[b] | −112.9 | −113.2 |
| 310 | −35(8) | −41.9 | −41.4 | −46.8[b] | −48.1[b] | −43.9[b] | −54.3[b] | −46.8[b] | −38.0 | 0.0[b] | −36.4 | −39.2 |
| 222 | −72(12) | −69.6 | −70.5 | −78.3 | −79.0 | −72.5 | −91.2[b] | −81.5 | −67.3 | 5.5[b] | −63.4 | −67.0 |
| 321 | 34(8) | 31.5 | 32.1 | 31.4 | 33.5 | 32.9 | 34.6 | 24.2[b] | 34.5 | 27.5 | 31.0 | 31.4 |
| 400 | 4(10) | 5.3 | 6.2 | 7.5 | 8.9 | 6.3 | 11.8 | 24.8[b] | 3.8 | −24.4[b] | 2.8 | 4.0 |
| 411 | 9(8) | 12.8 | 12.6 | 12.8 | 13.8 | 13.4 | 14.2 | 9.4 | 13.5 | 10.9 | 12.0 | 12.4 |
| 330 | 57(10) | 55.3 | 54.7 | 54.6 | 56.3 | 56.9 | 57.7 | 27.1[b] | 61.6 | 61.1 | 55.8 | 55.9 |
| 420 | −22(7) | −19.8 | −19.7 | −20.8 | −21.4 | −20.3 | −23.3 | −15.1 | −19.9 | 2.7[b] | −18.6 | −19.3 |
| 332 | 18(7) | 20.3 | 20.6 | 19.9 | 21.4 | 21.3 | 21.8 | 15.4 | 23.2 | 24.7 | 20.3 | 20.5 |
| 112 | −18(8) | −23.1 | −23.0 | −24.5 | −25.0 | −23.9 | −27.4 | −20.8 | −23.7 | −13.6 | −22.0 | −22.9 |
| 431 | 1(6) | 1.1 | 1.7 | −0.7 | 0.6 | 1.6 | −1.6 | −4.3 | 3.4 | 13.7[b] | 2.1 | 1.6 |
| 510 | −6(8) | −4.1 | −4.1 | −4.6 | −4.6 | −4.2 | −5.4 | −6.5 | −3.9 | −2.7 | −3.7 | −3.9 |
| 521 | 23(5) | 23.4 | 23.2 | 23.8 | 24.5 | 24.0 | 26.1 | 17.5 | 25.2 | 19.2 | 22.9 | 23.3 |
| 440 | 27(11) | 27.7 | 27.9 | 26.7 | 28.0 | 28.4 | 28.5 | 16.9 | 31.8 | 35.9 | 28.3 | 28.2 |
| 433 | 10(7) | 8.8 | 9.0 | 8.3 | 8.9 | 9.2 | 8.6 | 2.8 | 10.3 | 10.9 | 9.1 | 9.0 |
| 530 | −10(10) | −5.4 | −5.1 | −6.4 | −5.7 | −5.1 | −7.2 | −5.5 | −4.7 | 2.7[b] | −4.9 | −5.2 |
| 442 | 17(8) | 15.6 | 15.5 | 16.0 | 16.3 | 15.9 | 17.6 | 11.8 | 16.8 | 13.7 | 15.4 | 15.6 |
| 600 | 10(12) | 7.7 | 7.7 | 9.4 | 9.1 | 7.7 | 11.9 | 15.5 | 7.2 | −8.2[b] | 6.7 | 7.3 |
| 532 | −20(5) | −21.1 | −21.1 | −21.2 | −21.5 | −21.4 | −22.5 | −10.9[b] | −22.7 | −21.7 | −21.1 | −21.2 |
| 611 | −23(7) | −21.5 | −21.4 | −22.6 | −22.7 | −21.8 | −25.1 | −17.5 | −22.3 | −13.6[b] | −20.7 | −21.3 |
| 620 | 10(7) | 7.3 | 7.4 | 7.2 | 7.5 | 7.5 | 7.7 | 4.3 | 8.4 | 8.2 | 7.5 | 7.5 |
| 541 | −1(6) | −2.7 | −2.5 | −3.4 | −3.0 | −2.6 | −4.0 | −3.9 | −2.1 | 2.7 | −2.3 | −2.6 |
| 622 | 3(6) | 3.5 | 3.5 | 3.4 | 3.4 | 3.5 | 3.5 | 0.4 | 3.9 | 2.7 | 3.5 | 3.5 |
| 631 | 5(6) | 5.0 | 5.0 | 5.0 | 5.1 | 5.1 | 5.3 | 2.5 | 5.7 | 5.5 | 5.1 | 5.1 |
| 444 | 0(11) | 3.9 | 4.1 | 3.7 | 4.4 | 4.2 | 4.6 | 6.0 | 4.7 | 0.0 | 3.8 | 3.9 |
| 550 | 23(10) | 27.9 | 27.8 | 27.6 | 28.6 | 28.7 | 29.5 | 16.2 | 31.0 | 30.3 | 28.0 | 28.2 |
| 543 | −2(6) | −4.9 | −4.9 | −5.0 | −5.2 | −5.0 | −5.7 | −5.0 | −5.2 | −2.7 | −4.7 | −4.8 |
| 710 | −3(8) | 3.1 | 3.0 | 3.3 | 3.2 | 3.1 | 3.7 | 2.2 | 3.1 | 0.0 | 2.9 | 3.0 |

[a] The data of Schweika and Haubold from [47].
[b] The value of a SRO parameter that does not belong to the appropriate confidence interval of the Monte Carlo method (see MC column).

Note that, due to the comparatively large size of the confidence intervals of the Monte Carlo method in the case of the $Ni_{0.89}Cr_{0.11}$ alloy†, one may not consider the belonging of the SRO parameters values obtained within some approximation to these intervals as an evidence of high numerical accuracy of approximation. Moreover, on the basis of the previous results concerning both the high numerical accuracy of the ring approximation in the case of short-range atomic interactions and the tendency of this accuracy to enhance with increase of the characteristic radius of interactions, just the ring approximation data (rather than the Monte Carlo ones) may be considered as a standard in the case of the $Ni_{0.89}Cr_{0.11}$ alloy.

† As well as due to the absence of the corresponding test on the elimination of the boundary condition effect.

## 6. Summary and conclusions

On the basis of the performed comparative study of the numerical accuracy of the approximations, one can conclude the following.

At the calculations of the SRO parameters, the ring (1.2) approximation demonstrates high numerical accuracy of results in wide temperature and concentration intervals for alloys with both short- and long-range atomic interactions. The numerical adequacy of this approximation rises when the composition of alloy approaches the equiatomic value as well as with an increase of the characteristic radius of atomic interactions. All the foregoing, taking into account the comparative analytical simplicity of the ring approximation, ensures its effective use in the statistical–thermodynamic description of actual alloys and other lattice systems (for instance, semiconductors and magnetics) including those with a long-range character of atomic interactions‡.

The transition in consideration from the canonical ensemble to the grand canonical one in the statistical–thermodynamic description within the framework of all approximations listed in section 1 yields usually considerable rise of the numerical accuracy of the results. Only in the case of comparatively low concentrations (for the modified low-concentration Krivoglaz approximation at any concentration), the results weakly depend (or do not depend at all) on the type of statistical ensemble being used (see section 3). The use of normalization by multiplier (3.5) instead of normalization by summands (3.1) within the canonical ensemble results in considerably less rise of the numerical accuracy of approximations than the use of the grand canonical ensemble. Moreover, in a number of cases, the use of a multiplier normalization results in a decrease of the numerical accuracy.

In the framework of the lattice gas model, within the thermodynamic perturbation theory, the choice of the inverse effective number of atoms interacting with one fixed atom as a small parameter of the cumulant expansion along with taking account of the contributions from only linked irreducible diagrams ensures the fastest convergence of the cumulant expansion. Such an approach leads to the well known spherical model approximation (1.1) and to the new, high-accuracy ring (1.2) approximations. Taking into account the contributions from the reducible diagrams in the cumulant expansion (as in the chain approximation (1.4)) as well as the choice of the inverse temperature or the concentration of the impurity component (as in the modified Semenovskaya (1.3) and Krivoglaz low-concentration (1.5) approximations, respectively) as a small parameter of expansion results in a comparatively slower convergence of the cumulant expansion.

The results obtained within the spherical model approximation (1.1), modified Semenovskaya (1.3) and Tahir-Kheli [27] approximations demonstrate the high numerical accuracy in wide (but comparatively narrower than that of the ring approximation) concentration intervals near the equiatomic composition, and the width of such intervals enlarges with the increase of the effective radius of atomic interactions.

The cluster-variation method in the tetrahedral approximation [30, 31] gives adequate results in a wide temperature interval in two considered cases of the short-range interatomic potentials, for which the corresponding table data on the SRO parameters are available. However, the numerical accuracy of this method is lower than that of the ring, spherical model and Tokar–Masanskii–Grishchenko [12, 34] approximations. The accuracy of the results of this method becomes higher when the composition of the alloy decreases.

The Christy–Hall [35] approximation gives high-accuracy results for SRO parameters

‡ In [48], on the basis of a comparison with the results of the cluster-variation and Monte Carlo methods, a correct description of the temperature–concentration dependence of the Fourier transform of the SRO parameters within the framework of the ring approximation is demonstrated.

only for coordination shells with nonzero values of atomic interactions in the case of low concentrations. Its numerical accuracy is enhanced with the increase of the effective radius of atomic interactions.

The Krivoglaz–Clapp–Moss formula [18, 19, 21, 22, 26] demonstrates a very low numerical accuracy of results at all considered temperatures, compositions and types of the mixing potential. However, the numerical accuracy of its results has the tendency to increase, when the characteristic radius of atomic interactions enlarges as well as at a decrease of the concentration.

The chain (1.4) approximation demonstrates very low numerical accuracy of results at all considered temperatures, compositions and types of mixing potential.

The use of the Tokar–Masanskii–Grishchenko† [12, 34], modified Krivoglaz low-concentration (1.5), Vaks–Zein–Kamyshenko two-cluster and 4–2-cluster [33] approximations yields results of both high and low numerical accuracy. Unfortunately, it seems to be unfeasible to evaluate the limits (concerning the temperature, concentration and the effective radius of atomic interactions) of the correct applicability of these approximations on the basis of the consideration performed in the present work.

It should be noted that among all the considered approximations, only the chain (1.4), modified Krivoglaz low-concentration (1.5) and Vaks–Zein–Kamyshenko 4–2-cluster [33] ones are not invariant with respect to the transformation $c \to (1 - c)$. Thus, within these approximations the initial symmetry of the Hamiltonian is not saved [32]. This fact may be considered as one of the explanations for the low numerical accuracy of these approximations in a number of cases.

All approximations discussed in the present paper may be divided into two groups. The approximations from the first group (namely, the spherical model, ring, modified Semenovskaya, chain, Tokar–Masanskii–Grishchenko, Tahir-Kheli and Krivoglaz–Clapp–Moss ones) require the knowledge of the Fourier transform of the mixing potential to carry out the calculations, whereas those from the second group (namely, the Monte Carlo and cluster-variation methods as well as the modified Krivoglaz low-concentration, Christy–Hall and Vaks–Zein–Kamyshenko approximations) require the representation of the mixing potential in real space form. It should be noted that the 'real space' statistical–thermodynamic approximations have several disadvantages as compared to the 'reciprocal space' ones in a description of actual alloys with a long-range character of atomic interactions. Firstly, within the Monte Carlo and cluster-variation methods, the 'real space' calculations have a strong tendency to become more complicated with an increase of the effective radius of atomic interactions. Secondly, all the 'real space' statistical–thermodynamic approximations have a *principal* disadvantage, because they approximate the mixing potential by its values for a *finite* number of coordination shells, whereas such a specific feature of the mixing potential of actual alloys as the nonanalyticity of its Fourier transform (see e.g. [23–25, 50]) cannot be described in terms of the values of the mixing potential for any great but finite number of coordination shells.

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† In [49], both analytical and numerical comparative studies of the ring and Tokar–Masanskii–Grishchenko approximations are performed.

their values for any great but finite number of coordination shells. The authors thank Dr V M Nadutov for constant support during this research. The support from the Foundation of the Fundamental Investigations of Ukraine through grants No 2.4/965 and No 2.4/993 and from STCU through grant No 120 is gratefully acknowledged.

## References

[1] Chepulskii R V and Bugaev V N 1998 *J. Phys.: Condens. Matter* **10** 7309–26
[2] Cowley J M 1950 *Phys. Rev.* **77** 669
[3] Warren B E 1969 *X-ray Diffraction* (Reading, MA: Addison-Wesley)
[4] Berlin T H and Kac M 1952 *Phys. Rev.* **86** 821
[5] Brout R 1960 *Phys. Rev.* **118** 1009
[6] Brout R 1961 *Phys. Rev.* **122** 469
[7] Brout R 1965 *Phase Transitions* (New York: Benjamin)
[8] Philhours J and Hall G L 1968 *Phys. Rev.* **170** 496
[9] Hoffman D W 1972 *Metall. Trans.* **3** 3231
[10] Joyce G S 1972 *Phase Transitions and Critical Phenomena* vol 2, ed C Domb and M S Green (London: Academic) p 375
[11] Ziman J M 1979 *Models of Disorder* (Cambridge: Cambridge University Press)
[12] Tokar V I, Masanskii I V and Grishchenko T A 1990 *J. Phys.: Condens. Matter* **2** 10 199
[13] Yukhnovskii I R and Gurskii Z A 1991 *Quantum Statistical Theory of Disordered Systems* (Kiev: Naukova Dumka) (in Russian)
[14] Yukhnovskii I R, Gurskii Z A and Chushak Ya G 1991 *Phys. Status Solidi* b **163** 107
[15] Chepulskii R V and Bugaev V N 1998 *Solid State Commun.* **105** 615
[16] Semenovskaya S V 1978 *Phys. Status Solidi* b **87** 733
[17] Krivoglaz M A 1957 *Zh. Fiz. Khim.* **31** 1930
[18] Krivoglaz M A and Smirnov A A 1964 *The Theory of Order–Disorder in Alloys* (London: Macdonald)
[19] Krivoglaz M A 1969 *The Theory of X-ray and Thermal Neutron Scattering From Real Crystals* (New York: Plenum)
[20] Binder K (ed) 1979 *Monte Carlo Methods in Statistical Physics* (Heidelberg: Springer)
[21] Clapp P C and Moss S C 1966 *Phys. Rev.* **142** 418
[22] Clapp P C and Moss S C 1968 *Phys. Rev.* **171** 754
[23] Khachaturyan A G 1978 *J. Prog. Mater. Sci.* **22** 1
[24] Khachaturyan A G 1983 *Theory of Structural Transformations in Solids* (New York: Wiley)
[25] de Fontaine D 1979 *Solid State Physics* vol 34, ed H Ehrenreich, F Seitz and D Turnbull (New York: Academic) p 73
[26] Krivoglaz M A 1957 *Zh. Eksp. Teor. Fiz.* **32** 1368 (Engl. Transl. *Sov. Phys. JETP* **5** 1115)]
[27] Tahir-Kheli R A 1969 *Phys. Rev.* **188** 1142
[28] Philhours J and Hall G L 1967 *Phys. Rev.* **163** 460
[29] Balescu R 1975 *Equilibrium and Nonequilibrium Statistical Mechanics* (New York: Wiley)
[30] Golosov N S, Popov L E and Pudan L Ya 1973 *J. Phys. Chem. Solids* **34** 1149
[31] Golosov N S, Popov L E and Pudan L Ya 1973 *J. Phys. Chem. Solids* **34** 1157
[32] Chepulskii R V 1998 *J. Phys.: Condens. Matter* **10** 1505
[33] Vaks V G, Zein N E and Kamyshenko V V 1988 *J. Phys. F: Met. Phys.* **18** 1641
[34] Masanskii I V, Tokar V I and Grishchenko T A 1991 *Phys. Rev.* B **44** 4647
[35] Christy D O and Hall G L 1963 *Phys. Rev.* **132** 1958
[36] Fowler R H and Guggenheim E A 1952 *Statistical Thermodynamics* (Cambridge: Cambridge University Press)
[37] Guggenheim E A 1952 *Mixtures* (Oxford: Clarendon)
[38] Bichara C, Bergman C, Gaspard J P and Mathieu J C 1982 *Scr. Metall.* **16** 1121
[39] Kikuchi R and Sato H 1974 *Acta Metall.* **22** 1099
[40] Sanchez J M and de Fontaine D 1978 *Phys. Rev.* B **17** 2926
[41] Sanchez J M 1982 *Physica* A **111** 200
[42] Sanchez J M, Ducastelle F and Gratias D 1984 *Physica* A **128** 334
[43] Mohri T, Sanchez J M and de Fontaine D 1985 *Acta Metall.* **33** 1463
[44] Ducastelle F 1991 *Order and Phase Stability in Alloys* (New York: Elsevier)

[45] de Fontaine D 1994 *Solid State Physics* vol 47, ed H Ehrenreich, F Seitz and D Turnbull (New York: Academic) p 33
[46] Sanchez J M, Pierron-Bohnes V and Mejia-Lira F 1995 *Phys. Rev.* B **51** 3429
[47] Schweika W and Haubold H-G 1988 *Phys. Rev.* B **37** 9240
[48] Chepulskii R V and Bugaev V N 1998 *J. Phys. Chem. Solids* at press
[49] Chepulskii R V 1998 *J. Phys. Chem. Solids* at press
[50] Bugaev V N and Tatarenko V A 1989 *Interaction and Arrangement of Atoms in Interstitial Solid Solutions Based on Close-Packed Metals* (Kiev: Naukova Dumka) (in Russian)