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COMPARISON OF TWO ANALYTICAL APPROXIMATIONS FOR CALCULATION OF THE SHORT-RANGE ORDER IN DISORDERED ALLOYS

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Abstract—Both analytical and numerical comparative studies of two high-accuracy approximations elaborated recently by Tokar *et al.* (*J. Phys.: Condens. Matter*, 1990, **2**, 10199) and by Chepulskii and Bugaev (*Solid State Commun.*, 1998, **105,** 615) for calculation of the short-range order parameters in binary disordered alloys are performed. It is shown that, under additional assumptions, one of these approximations may be presented in a form analogous to that of the other approximation. By means of comparison with the results of the Monte Carlo simulation, the approximation which demonstrates the higher numerical accuracy in actual alloys with long-range characters of atomic interactions is found. © 1998 Elsevier Science Ltd. All rights reserved

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1. INTRODUCTION

In recent papers [1–4], two high-accuracy analytical approximations for the calculation of the short-range order (SRO) parameters in binary disordered alloys with a Bravais crystal lattice have been developed. One such approximation [1, 2] [hereafter referred to as the Tokar–Masanskii–Grishchenko (TMG) approximation] is based on application of the γ-expansion method [5] with the choice of the quantity $\gamma = \exp(-1/\xi)$, where ξ is the effective radius of interatomic correlations, as a small parameter of expansion. The other approximation [3, 4] (hereafter referred to as the ring approximation [4]†) is based on the application of a modified thermodynamic perturbation theory with the choice of the inverse effective number of atoms interacting with one fixed atom as a small parameter of expansion. The aim of the present paper is both analytical and numerical comparative studies of these two approximations.

2. RESULTS AND DISCUSSION

Firstly, let us show that, under the additional assumptions, the ring approximation may be presented in a form analogous to that of the TMG approximation. For this purpose, the following equivalent form of the expression for the Fourier transform $\alpha_{\mathbf{k}}^{\text{ring}}$ of the SRO parameters derived within the framework of the ring approximation is convenient:

$$\alpha_{\mathbf{k}}^{\text{ring}} = \left[\tilde{F}_{\mathbf{k}}^{-1} - c_1 + N^{-1}\textstyle\sum_{\mathbf{q}}\tilde{F}_{\mathbf{q}}\left(c_2 - c_3\tilde{F}_{\mathbf{k}-\mathbf{q}}\right)\right]^{-1}$$

$$= \left[\tilde{F}_{\mathbf{k}}^{-1} - c_1 + c_2 F_{\mathbf{R}=0} - c_3\sum_{\mathbf{R}}(F_{\mathbf{R}})^2\exp(-i\mathbf{k}\mathbf{R})\right]^{-1}, \tag{1}$$

where

$$c_1 = \frac{1-2c(1-c)}{2c(1-c)}, c_2 = \frac{1-3c(1-c)}{c(1-c)}, c_3 = \frac{(1-2c)^2}{2c(1-c)},$$

$$\tilde{F}_{\mathbf{k}} = \left[1 + c(1-c)\left(\tilde{V}_{\mathbf{k}} + \mu_{\text{ring}}\right)/(k_{\text{B}}T)\right]^{-1},$$

$$F_{\mathbf{R}} = N^{-1}\sum_{\mathbf{q}}\tilde{F}_{\mathbf{q}}\exp(i\mathbf{q}\mathbf{R}), \tag{2}$$

$\tilde{V}_{\mathbf{k}}$ is the Fourier transform of pair mixing potential, T is the absolute temperature, k_{B} is the Boltzmann constant, c is the concentration, N is the number of sites in the alloy crystal lattice, the summation on $\mathbf{q}$ is over all points in the first Brillouin zone specified by the cyclic boundary conditions and the quantity μ_{ring} should be determined from the equation:

$$N^{-1}\sum_{\mathbf{q}}\alpha_{\mathbf{q}}^{\text{ring}} = 1. \tag{3}$$

By intrduction the quantity $\Sigma_{\mathbf{R}}$ (not to be confused with the summation $\sum_{\mathbf{R}}$)

$$-c(1-c)\textstyle\sum_{\mathbf{R}} = \delta_{\mathbf{R},0}\left[1 - c_1 + c_2F_{\mathbf{R}=0} + \dfrac{c(1-c)}{k_{\text{B}}T}\mu_{\text{ring}}\right] - c_3(F_{\mathbf{R}})^2 \tag{4}$$

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†This name of the approximation is in accordance with the topology of the diagrams corresponding to the additional (with respect to the SM approximation) sums taken into account in the cumulant expansion within the diagrammatic technique developed in Ref. [4].

($\delta_{\mathbf{R},0}$ is the Kronecker delta), the expression (1) may be rewritten as follows:

$$\alpha_{\mathbf{k}}^{\text{ring}} = \left\{ \frac{c(1-c)}{k_{\text{B}}T}\tilde{V}_{\mathbf{k}} - c(1-c)\sum_{\mathbf{R}}\left[\sum\nolimits_{\mathbf{R}}\exp(-i\mathbf{kR})\right] \right\}^{-1} \tag{5}$$

In Refs. [3, 4], it was shown that, sufficiently far from the critical region and/or in the case of a sufficiently large effective radius of atomic interactions, the results obtained within the framework of the spherical model (SM) approximation [1, 3, 4, 6–10]:‡

$$\alpha_{\mathbf{k}}^{\text{SM}} = \left[1 + c(1-c)\left(\tilde{V}_{\mathbf{k}} + \mu_{\text{SM}}\right)/(k_{\text{B}}T)\right]^{-1}, \tag{6}$$

[where the quantity μ_{SM} should be determined from eqn (3) under the substitution of $\alpha_{\mathbf{k}}^{\text{SM}}$ instead of $\alpha_{\mathbf{k}}^{\text{ring}}$] are closed to the corresponding results of the ring approximation:

$$\alpha_{\mathbf{k}}^{\text{SM}} \approx \alpha_{\mathbf{k}}^{\text{ring}},\ \mu_{\text{SM}} \approx \mu_{\text{ring}}. \tag{7}$$

In the case of eqn (7), from eqns (2) and (4) we obtain

$$F_{\mathbf{R}} \approx \alpha_{\mathbf{R}}^{\text{SM}} \approx \alpha_{\mathbf{R}}^{\text{ring}}$$

$$\Sigma_{\mathbf{R}\neq 0} \approx A\left(\alpha_{\mathbf{R}}^{\text{ring}}\right)^2, \tag{8}$$

where

$$A = \frac{c_3}{c(1-c)} = \frac{1}{2}\left[\frac{1-2c}{c(1-c)}\right]^2 \tag{9}$$

and the quantity $\Sigma_{\mathbf{R}=0}$ should be determined from eqn (3).

The initial expression obtained within the framework of the γ-expansion method [1, 2, 12, 13] coincides with that of the ring approximation (5), in which, however,

$$\Sigma_{\mathbf{R}\neq 0} = A\left(\alpha_{\mathbf{R}}^{\text{ring}}\right)^2 + B\left(\alpha_{\mathbf{R}}^{\text{ring}}\right)^3 + O\left(\alpha^4\right), \tag{10}$$

where the quantity A is the same as in eqn (9) and B is another function of concentration. It is obvious that the approximation (8) (derived from the ring approximation under the additional assumptions) coincides with eqn (10) neglecting all the sums proportional to the powers of the quantities $\alpha_{\mathbf{R}}$ more than the second power.

Unfortunately, within the framework of both approximations [eqns (5) and (8)] and [eqns (5) and (10)], the solution of the direct problem of calculation of the SRO parameters for a given type of mixing potential is not feasible, because it requires one to solve an *infinite* set of non-linear integral equations. Only the assumption of a small value of the effective radius of interatomic correlations allows us to decrease the order of this set of equations, leading to the TMG approximation [1, 2]:

$$\Sigma_{\mathbf{R}_1} = A(\alpha_{\mathbf{R}_1})^2 + B(\alpha_{\mathbf{R}_1})^3,$$

$$\Sigma_{\mathbf{R}_{2,3}} = A(\alpha_{\mathbf{R}_{2,3}})^2,$$

$$\Sigma_{\mathbf{R}_s} = 0 \text{ for } s > 3, \tag{11}$$

where $\mathbf{R}_s$ is the radius vector of a site within the sth coordination shell. It should be emphasized that, to solve the direct problem within the framework of the initial ring approximation (1), it is necessary to solve no more than one (like within the spherical model approximation) non-linear integral equation (3), since the SRO parameters do not appear on the right-hand side of the corresponding expression (1).

To study the relative numerical accuracy of the ring (1) and TMG [eqns (5) and (11)] approximations, a comparison of the values of the SRO parameters for the first four coordination shells of a face-centred cubic (f.c.c.) crystal lattice calculated within the framework of these two approximations was made with the corresponding data using the Monte Carlo method. In the eight considered cases for each of the concentrations 0.01, 0.10, 0.25 and 0.50,§ two model types of the mixing potential were used: (a) $V_1 > 0$, $V_s = 0$ ($s > 1$) and (b) $V_1 > 0$, $V_2 = -0.5V_1$, $V_s = 0$ ($s > 2$) (V_s is the mixing potential for the sth coordination shell). Such a choice permits us to reveal the tendencies in the change of the numerical accuracy of approximations with variation of both the concentration and the effective radius of atomic interactions.

In Fig. 1, the results obtained in two cases corresponding to $c = 0.10$ taking into consideration the atomic interactions for one [Fig. 1(a)] and two [Fig. 1(b)] coordination shells are shown. The point T_0 of the phase transition corresponds to the point of inflection [Fig. 1(a), $T_0 = 0.35(5)$] or to the abrupt change [Fig. 1(b), $T_0 = 0.615(5)$] of the temperature dependence of the SRO parameters obtained by the Monte Carlo method. Note that, in the case of $V_2 \neq 0$ [Fig. 1(b)], the solution of the problem within the TMG approximation does not exist for reduced temperatures less than 0.91.

The spherical model approximation (6) is the zeroth order approximation within the framework of both the γ-expansion method [1, 2] and a modified thermodynamic perturbation theory [3, 4]. Because of this, the results obtained within the framework of the spherical model approximation were also included and are shown in Fig. 1 to help one to examine the convergence of two corresponding perturbation series expansions.

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‡It is notable that the mean field with Onsager corrections approximation derived in Ref. [11] coincides (see Ref. [8]) with the spherical model approximation.

§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 $c \rightarrow (1-c)$ [14].

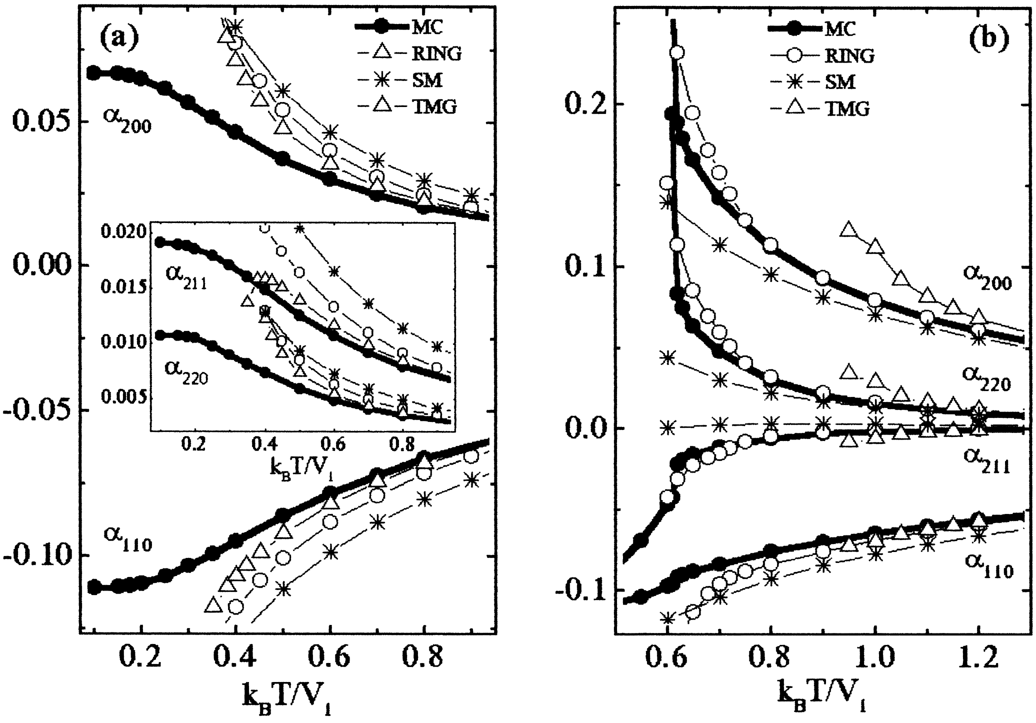

Fig. 1. The dependencies of the short-range order parameters for the first four coordination shells of the f.c.c. crystal lattice on the reduced temperature obtained by simulation with the Monte Carlo method (MC) as well as within the framework of the ring (RING), spherical model (SM) and Tokar–Masanskii–Grishchenko (TMG) approximations at $c = 0.10$, $V_1 > 0$, $V_s = 0$ ($s > 2$) and $V_2 = 0$ (a) and $V_2 = -0.5V_1$ (b). In case (b), for $k_BT/V_1 < 0.91$, the solution of the problem within the TMG approximation does not exist.

As a result of the numerical study based on the acceptance of the Monte Carlo simulation data as a standard, the following was found.

In all cases considered, corresponding to the account of atomic interactions only for the first coordination shell, the numerical accuracy of the ring approximation is somewhat disadvantageous in relation to the TMG approximation's accuracy [see, e.g., Fig. 1(a)]. When the atomic interactions for the first two coordination shells are taken into account, the numerical accuracy of the ring approximation proves to be higher (and considerably higher at $c = 0.01$ and $c = 0.10$) than the accuracy of the TMG approximation [see, e.g., Fig. 1(b)]. The results of both approximations aymptotically approach one another when c → 0.5 and *vice versa* when c → 0.

In all cases considered, the numerical accuracy of the spherical model approximation proves to be lower than that of the ring approximation, but it may be both higher and lower than the accuracy of the TMG approximation.

3. CONCLUSION

From the results obtained in the present work, it follows that in the case of the long-range character of atomic interactions in alloys, the choice of the inverse effective number of atoms interacting with one fixed atom (like in the ring approximation) is more appropriate than the choice of the quantity $\gamma = exp(-1/\xi)$, where ξ is the effective radius of interatomic correlations (as in the TMG approximation), as a small parameter of a corresponding perturbation theory.|| Because atomic interactions in actual alloys are found to have only long-range character (for review see, e.g., Ref. [4]), the ring approximation should be primarily recommended for a correct statistical thermodynamic description of the short-range order in such alloys.

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||Note that the revealed bad convergence of the field theoretical perturbation series within the TMG approximation may be explained by the asymptotic character of this series [13, 15].

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