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ANALYTICAL METHOD FOR CALCULATION OF THE SHORT-RANGE ORDER IN ALLOYS

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A new simple analytical approximation for calculations of the short-range order parameters and their Fourier transform in disordered binary alloys with a Bravais crystal lattice and with atomic interactions of arbitrary effective radius of action is proposed. On the basis of the comparison with the Monte Carlo simulation data, the high numerical accuracy of approximation is demonstrated and it is shown that this accuracy turns higher with the increase of the effective radius of atomic interactions. The developed approach may be also followed in studies of magnetics within the framework of the Izing model, of fluids and amorphous materials within the lattice gas model as well as in investigations of the low-dimension lattice systems. © 1998 Elsevier Science Ltd

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Currently, there exist a number of analytical approaches for calculations of the short-range order parameters in disordered (i.e. without a long-range order) binary alloys (for overview see Refs 1–5). One of the comparatively simple in a practical implementation but methodologically consistent approach is based on the joint application of the thermodynamic perturbation theory and the fluctuation method [1–4, 6–9]. The important advantage of such approach is the potentiality of taking into account the long-range contributions into atomic interactions without a sizeable complication of a consideration.

By now, the essential disadvantage of the joint application of the thermodynamic perturbation theory and the fluctuation method in alloy studies lies in taking account of only the finite (as a rule small) number of terms in a perturbation series under the choice of the inverse temperature as a small parameter of expansion, whereas the convergence of this series is relatively weak. At the same time, the considerable progress in the development of the thermodynamic perturbation theory within the Izing model was achieved in the works of Brout [10–13], where the possibility of analytical summation of the infinite number of terms that mainly contributes into the corresponding series was demonstrated in the realistic case of long-range atomic interactions. In this case, the value reciprocal to the effective radius of atomic interactions was chosen as a small parameter of expansion. However, such approach has not found the deserved applications in alloy studies, and nothing more than two corresponding works [14, 15] are familiar to us.

Besides, thus far, the thermodynamic perturbation theory was applied in alloy studies within the framework of the canonical ensemble only. At the same time, it is known [16, 17] that, within the approximate methods (unlike the rigorous ones), the step from the canonical ensemble to the grand canonical one may ensure the rise of the numerical accuracy of calculations of thermodynamic characteristics. Moreover, as a result of such step, one may expect the rise of the accuracy of the thermodynamic fluctuation method itself, because, within the grand canonical ensemble, the fluctuations of the occupation probabilities for the different sites of an alloy crystal lattice are not constrained by the requirement of the constancy of the

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total number of alloy atoms and, hence, these fluctuations are absolutely independent of one another. Thus, within the grand canonical ensemble, the necessary condition of the usability of the thermodynamic fluctuation method [18] is satisfied in contradiction to the case of the canonical ensemble, when the abovementioned requirement takes place.

The aim of the present study is to propose the new analytical method for calculations of the short-range order parameters in disordered binary alloys with a Bravais crystal lattice based on the joint application of the thermodynamic fluctuation method and perturbation theory within the grand canonical ensemble, adopting the inverse effective radius of atomic interactions as a small parameter of expansion.

In general case, within the framework of the lattice gas model, the hamiltonian H of a two-component A–B alloy with a Bravais crystal lattice and with atomic interactions of less than or equal to the second order can be written in the following form [19,20]

$$H = Nv_0 + \Phi \sum_{\mathbf{R}} C_{\mathbf{R}} + 1/2 \sum_{\mathbf{R}_1,\mathbf{R}_2} V_{\mathbf{R}_1-\mathbf{R}_2} C_{\mathbf{R}_1} C_{\mathbf{R}_2}. \qquad (1)$$

In (2.1): v_0 is the energy per site of alloy in which all N sites are occupied by B-sort atoms; Φ is the potential of the injection of an A-sort atom into a crystal lattice site (the unary mixing potential); $V_{\mathbf{R}_1-\mathbf{R}_2}$ is the binary mixing potential;

$$C_{\mathbf{R}} = \begin{cases} 1, \text{if an A}-\text{sort atom is at site } \mathbf{R} \\ 0, \text{otherwise} \end{cases}; \qquad (2)$$

the summations on the vectors $\mathbf{R}$, $\mathbf{R}_1$ and $\mathbf{R}_2$ are carried over all crystal lattice sites. The expression for the grand thermodynamic potential Ω of the system in question may be presented in the following form [21]

$$\Omega = \Omega_0 - k_B T \ln \Delta\Gamma + \Delta\Omega, \qquad (3)$$

where

$$\Omega_0 = N\left(v_0 - \mu_{\mathrm{B}}\right), \qquad (4)$$

$$\Delta\Omega = -k_B T \times \ln\left\langle \exp\left[-(2k_BT)^{-1} \sum_{\mathbf{R}_1,\mathbf{R}_2} W_{\mathbf{R}_1-\mathbf{R}_2} C_{\mathbf{R}_1} C_{\mathbf{R}_2}\right]\right\rangle, \qquad (5)$$

$$W_{\mathbf{R}_1-\mathbf{R}_2} = V_{\mathbf{R}_1-\mathbf{R}_2} + \mu\delta_{\mathbf{R}_1,\mathbf{R}_2}, \qquad (6)$$

$$\mu = 2\left(\Phi - \mu_{\mathrm{A}} + \mu_{\mathrm{B}}\right), \qquad (7)$$

μ_{A} and μ_{B} are the chemical potentials of A- and B-sort atoms, respectively, T is the absolute temperature, k_B is the Boltzmann constant, the sign $\langle\ldots\rangle$ means the statistical average over all states with given values of the long-range order parameters, $\delta_{\mathbf{R}_1,\mathbf{R}_2}$ is the Kronecker's delta,

$$\ln \Delta\Gamma = -\sum_{\mathbf{R}} \left[P_{\mathbf{R}} \ln P_{\mathbf{R}} + (1 - P_{\mathbf{R}}) \ln (1 - P_{\mathbf{R}})\right], \qquad (8)$$

$$P_{\mathbf{R}} = \langle C_{\mathbf{R}} \rangle \qquad (9)$$

and is equal to the probability of finding an A-sort atom at the site $\mathbf{R}$. Notice that the values of the chemical potentials μ_{A} and μ_{B} and, therefore [see (6,7)], the value of μ must satisfy the general thermodynamic relationships [18]

$$N_{\mathrm{A}} = -\left(\partial\Omega/\partial\mu_{\mathrm{A}}\right)_T, N_{\mathrm{B}} = -\left(\partial\Omega/\partial\mu_{\mathrm{B}}\right)_T. \qquad (10)$$

According to the general approach of the thermodynamic perturbation theory [3,10–13,22,23], the expression (5) for $\Delta\Omega$ may be expanded in a cumulant series in powers of the inverse temperature. Following to the Brout's [10–13] approach, let us select the contributions $\Omega^{(0)}$ and $\Omega^{(1)}$ to the cumulant expansion from the summands proportional, respectively, to zeroth and first powers of the quantity z^{-1}, where z is the number of sites within the imaginary shell whose radius is equal to the effective radius of interatomic interactions

$$\Omega^{(0)} = \Omega_0 + 1/2 \sum_{\mathbf{R}_1,\mathbf{R}_2} W_{\mathbf{R}_1-\mathbf{R}_2} P_{\mathbf{R}_1} P_{\mathbf{R}_2} - k_B T \ln \Delta\Gamma, \qquad (11)$$

$$\Omega^{(1)} = 1/2 \sum_{n=0}^{\infty} \left[(-k_BT)^n (n+1)\right]^{-1} \times \sum_{\mathbf{R}_1,\mathbf{R}_2,\ldots,\mathbf{R}_{n+1}} W_{\mathbf{R}_1-\mathbf{R}_2} W_{\mathbf{R}_2-\mathbf{R}_3} \ldots W_{\mathbf{R}_{n+1}-\mathbf{R}_1} \times \prod_{i=1}^{n+1} P_{\mathbf{R}_i}\left(1 - P_{\mathbf{R}_i}\right). \qquad (12)$$

In the case of the disordered state of alloy, when $P_{\mathbf{R}} = c = N_{\mathrm{A}}/N$ for any $\mathbf{R}$, we have

$$\Omega^{(0)} = \Omega_0 + Nc^2 \widetilde{W}_{\mathbf{k}=0}/2 + Nk_BT\left[c \ln c + (1 - c) \ln (1 - c)\right], \qquad (13)$$

$$\Omega^{(1)} = k_BT/2 \sum_{\mathbf{k}} \ln\left[1 + \widetilde{W}_{\mathbf{k}} c (1 - c) / (k_BT)\right], \qquad (14)$$

where

$$\widetilde{W}_{\mathbf{k}} = \widetilde{V}_{\mathbf{k}} + \mu, \qquad (15)$$

$$\widetilde{V}_{\mathbf{k}} = \sum_{\mathbf{R}} V_{\mathbf{R}} \exp(-i\mathbf{kR}) \qquad (16)$$

is the Fourier transform of the mixing potential $V_{\mathbf{R}}$ and the summation on $\mathbf{k}$ is carried over all the points

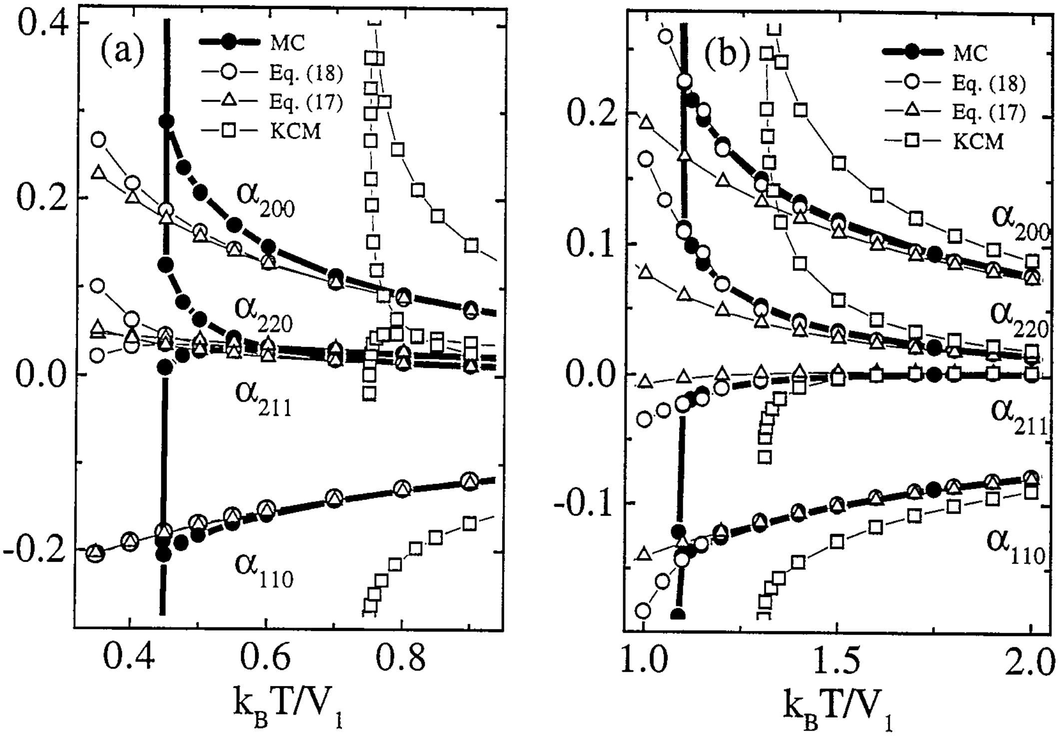

Fig. 1. The dependencies of the short-range order parameters for the first four coordination shells of the f. c. c. crystal lattice on the reduced temperature obtained within the framework of the Monte Carlo method (MC), Krivoglaz–Clapp–Moss formula (KCM) as well as approximations (17) and (18) at $c = 0.25$, $V_1 > 0$, $V_s = 0$ ($s > 2$) and (a) $V_2 = 0$, (b) $V_2 = -0.5V_1$ (V_s is the mixing potential for the s-th coordination shell).

specified by the cyclic boundary conditions in a corresponding first Brillouin zone. Note that the analogous to (14) expression was firstly obtained by Brout [11–13] (see also [15,24–27]).

Applying the thermodynamic fluctuation method [1–4, 18] to the expressions for $\Omega^{(0)}$ and $\Omega^{(0)} + \Omega^{(1)}$ and using (10), we obtain, respectively, two following approximate expressions

$$\alpha^{(0)}_{\mathbf{k}} = \left[1 + \widetilde{W}_{\mathbf{k}} c\,(1-c)\,/\,(k_BT)\right]^{-1}, \qquad (17)$$

$$\alpha^{(1)}_{\mathbf{k}} = \left[I + \widetilde{W}^{eff}_{\mathbf{k}} c\,(1-c)\,/\,(k_BT)\right]^{-1}, \qquad (18)$$

for the Fourier transform $\alpha_{\mathbf{k}}$ of the short-range order Warren–Cowley parameters $\alpha_{\mathbf{R}}$ [28]

$$\alpha_{\mathbf{k}} = \sum_{\mathbf{R}} \alpha_{\mathbf{R}} \exp\left(-i\mathbf{k}\mathbf{R}\right), \qquad (19)$$

$$\alpha_{\mathbf{R}_1-\mathbf{R}_2} = \left(\langle C_{\mathbf{R}_1} C_{\mathbf{R}_2}\rangle - c^2\right)\left[c\,(1-c)\right]^{-1} \qquad (20)$$

and

$$I = N^{-1}\sum_{\mathbf{q}}\left[1 + \widetilde{W}_{\mathbf{q}} c\,(1-c)\,/\,(k_BT)\right]^{-1}, \qquad (21)$$

$$\widetilde{W}^{eff}_{\mathbf{k}} = \widetilde{W}_{\mathbf{k}} - \frac{(1-2c)^2}{2k_BT} \times N^{-1}\sum_{\mathbf{q}} \widetilde{W}_{\mathbf{q}}\widetilde{W}_{\mathbf{k}-\mathbf{q}}\left[1 + \frac{c\,(1-c)}{k_BT}\widetilde{W}_{\mathbf{q}}\right]^{-1} \times \left[1 + \frac{c\,(1-c)}{k_BT}\widetilde{W}_{\mathbf{k}-\mathbf{q}}\right]^{-1}. \qquad (22)$$

In both expressions (17) and (18), μ is the quantity to be found from the equation

$$N^{-1}\sum_{\mathbf{q}} \alpha^{(i)}_{\mathbf{q}} = 1, \qquad (23)$$

at i=1 and 2, respectively. Notice that the expression (17) is identical to the well-known expression obtained within the spherical model [11–13,26,27,29–31].

To study the numerical accuracy of the derived approximations, in Fig. 1(a,b) the dependencies of the

SRO parameters for the first four coordination shells of the f. c. c. crystal lattice on the reduced temperature that were calculated by use of the equations (17) and (18) as well as through the Monte Carlo simulations [21, 32] and within the widely used Krivoglaz–Clapp–Moss [1, 2, 6, 33, 34] approximation are plotted at $c=0.25$. The temperature interval $[T_0, 2T_0]$ was considered (T_0 is the temperature of the order–disorder phase transition) and pair atomic interactions for one [Fig. 1(a)] or two [Fig. 1(b)] nearest coordination shells were taken into account.

From Fig. 1, accepting the results of the Monte Carlo simulations as a standard, one may conclude that the approximation (18) demonstrates the highest numerical accuracy of results, which considerably rises when the pair atomic interactions on the second coordination shell are taken into account (i.e. with an increase of the characteristic radius of atomic interactions). Note that in Ref. [21] the more complete study of the numerical accuracy of derived approximations is performed and the same conclusions are reached.

The above study of the numerical accuracy of the approximations elaborated in present paper testifies that comparatively simple analytical approximation (18) may be recommended for description in a wide temperature interval of SRO parameters in actual alloys for which the long-range contributions into atomic interactions are typical (for review see [21]). It is notable that within the framework of this approximation, the effective radius of atomic interactions is not limited *a priori* (as, for instance, within the Monte Carlo and cluster-variation methods), since for corresponding calculations it is necessary to know the Fourier transform of interatomic potentials.

Owing to the equivalence of the two-component lattice gas and Ising models [13], the obtained results may be also used in a research of magnetics. The absence of *a priori* assumptions about the space dimensionality of a crystal lattice in the developed formalism permits readily to apply it in investigations of low-dimension lattice systems, as well. The approximation elaborated in the present work may be also useful in the investigations of fluids and amorphous materials within the framework of the lattice gas model [13].

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