J. Phys.: Condens. Matter **11** (1999) 8645–8660. Printed in the UK PII: S0953-8984(99)04957-7

Analytical description of the short-range order in alloys with many-body atomic interactions. II

R V Chepulskii

Department of Solid State Theory, Institute for Metal Physics,
National Academy of Sciences of Ukraine, UA-252680 Kyiv-142, Ukraine

E-mail: `chep@imp.kiev.ua`

Received 3 June 1999

Abstract. The recently elaborated approach (Chepulskii R V and Bugaev V N 1998 *J. Phys.: Condens. Matter* **10** 7309–26, 7327–48) based on the joint application of the thermodynamic fluctuation method and perturbation theory is generalized to the case of the presence of not only pair but also nonpair atomic interactions of arbitrary orders in an alloy. Within such an approach, a number of new analytical approximations are derived for calculation of the grand thermodynamic potential as well as of the short-range order parameters and their Fourier transform in disordered binary alloys of arbitrary compositions and with Bravais crystal lattices. The effective radius of atomic interactions is not limited *a priori*. The inverse effective number of atoms interacting with one fixed atom as well as the inverse temperature are successively used as a small parameter of expansion. The developed approach may be also followed in studies of magnetics in the framework of the Ising model and of fluids and amorphous materials within the lattice gas model as well as in investigations of low-dimensional lattice systems.

1. Introduction

In [1]†, a number of analytical approximations were elaborated for calculation of the short-range order (SRO) parameters and their Fourier transform in disordered (i.e. without a long-range order (LRO)) binary alloys with Bravais crystal lattices and with many-body atomic interactions of arbitrary orders and effective radii of action. To achieve this aim, the Krivoglaz approach [2–5] based on application of the thermodynamic fluctuation method within the mean-field approximation was used. From all the obtained approximations, the generalized spherical model one yielded the highest numerical accuracy of results.

However, within the spherical model approximation, it is impossible to describe the phenomenon of temperature dependence of a position in reciprocal space of the SRO Fourier transform's maximum in the case of temperature independent atomic interactions. The presence of nonpair atomic interactions has no effect on this conclusion [1]. Thus, the use of this approximation is not adequate when the denoted phenomenon takes place, as, for instance, in Pd–V [6, 7], Cu–Au and Cu–Pd [8–12] as well as Pt–V [13–15] alloys and in a binary Madelung lattice [7, 16].

In the case of the *absence* of nonpair atomic interactions in an alloy, the denoted temperature dependence can be correctly (see [7]) described within the ring approximation,

---

† Despite the erroneous absence of the first number in the title of the previous paper [1], it is in fact the first part of the present work accordingly numbered as II.

0953-8984/99/448645+16$30.00

derived by use of the thermodynamic fluctuation method within the first order of a modified thermodynamic perturbation theory under the choice of the inverse effective number of atoms interacting with one fixed atom as a small parameter of expansion [17–20]. For such a description to be correct also in the case of alloys with nonpair atomic interactions (such as Cu–Au and Cu–Pd [8–10]), it seems to be useful to generalize the ring approximation to this case. The present paper is devoted to the performance of such a generalization.

In section 2, the expressions for both the grand partition function and the thermodynamic potential of the alloy in question are obtained in the framework of the lattice gas model.

In section 3, the traditional cumulant expansion in the thermodynamic perturbation theory within the lattice gas model is generalized to the case of the presence of many-body atomic interactions of arbitrary orders in the alloy and the corresponding diagram technique is developed.

In section 4, the expressions for both the grand thermodynamic potential and the SRO parameters are obtained within the high-temperature approximation that corresponds to the account of the terms in the cumulant expansion that are proportional to the zeroth power of the inverse temperature.

In section 5, the Brout classification of the terms in the cumulant expansion [21–24] is generalized to the case of the presence of many-body atomic interactions of arbitrary orders in the alloy.

In sections 6 and 7, the expressions for both the grand thermodynamic potential and the SRO parameters are obtained within the approximations that are appropriate to the account of the terms in the cumulant expansion that are proportional to the zeroth as well as zeroth and first powers of the inverse effective number of atoms interacting with one fixed atom.

In section 8, we describe the details of application of the obtained approximations in combination with three widely used approaches for calculation of interatomic potentials in alloys, the generalized perturbation [25–28] and Connolly–Williams [29, 30] methods as well as the mean-field concentration function theory [31–33].

In section 9, the symmetry aspects are discussed.

In section 10, the conclusions and perspectives are given.

2. Grand thermodynamic potential

In general, in the framework of the lattice gas model, the Hamiltonian H of a two-component A–B alloy with a Bravais crystal lattice and with many-body atomic interactions of arbitrary orders and radius of action can be written in the following form [1, 34–36]

$$\begin{aligned} H = N v_0 + \sum_{n=1}^{N} \frac{1}{n!} \sum_{\boldsymbol{R}_1,\boldsymbol{R}_2,\ldots,\boldsymbol{R}_n} V^{(n)}_{\boldsymbol{R}_1,\boldsymbol{R}_2,\ldots,\boldsymbol{R}_n} C_{\boldsymbol{R}_1} C_{\boldsymbol{R}_2} \ldots C_{\boldsymbol{R}_n} = N v_0 + \sum_{\boldsymbol{R}} V^{(1)}_{\boldsymbol{R}} C_{\boldsymbol{R}} \\ + \frac{1}{2} \sum_{\boldsymbol{R}_1,\boldsymbol{R}_2} V^{(2)}_{\boldsymbol{R}_1,\boldsymbol{R}_2} C_{\boldsymbol{R}_1} C_{\boldsymbol{R}_2} + \frac{1}{6} \sum_{\boldsymbol{R}_1,\boldsymbol{R}_2,\boldsymbol{R}_3} V^{(3)}_{\boldsymbol{R}_1,\boldsymbol{R}_2,\boldsymbol{R}_3} C_{\boldsymbol{R}_1} C_{\boldsymbol{R}_2} C_{\boldsymbol{R}_3} + \cdots . \end{aligned} \tag{2.1}$$

In (2.1) v_0 is the energy per site of an 'alloy' in which all N sites are occupied by B-type atoms,

$$C_{\boldsymbol{R}} = \begin{cases} 1 & \text{if the site } \boldsymbol{R} \text{ is occupied by an A-type atom} \\ 0 & \text{otherwise} \end{cases} \tag{2.2}$$

$\sum_{\boldsymbol{R}}$ means the summation over all N sites of the crystal lattice, $V^{(n)}_{\boldsymbol{R}_1,\boldsymbol{R}_2,\ldots,\boldsymbol{R}_n}$ is the mixing potential of nth order ($n = 1, 2, \ldots, N$) [1, 35, 36]

$$V^{(n)}_{\boldsymbol{R}_1,\boldsymbol{R}_2,\ldots,\boldsymbol{R}_n} = 0 \qquad \text{if } \boldsymbol{R}_i = \boldsymbol{R}_j \ (i, j = 1, 2, \ldots, n;\ i \neq j). \tag{2.3}$$

The grand partition function Ξ of the disordered alloy in question can be presented in the following form

$$\begin{aligned}\Xi &\equiv \sum_{\{C_{\boldsymbol{R}}\}} \exp[-(k_{\mathrm{B}}T)^{-1}(H - \mu_{\mathrm{A}}N_{\mathrm{A}} - \mu_{\mathrm{B}}N_{\mathrm{B}})] \\ &= \Xi_0 \sum_{\{C_{\boldsymbol{R}}\}} \exp\left[-(k_{\mathrm{B}}T)^{-1}\sum_{n=2}^{N}\frac{1}{n!}\sum_{\boldsymbol{R}_1,\boldsymbol{R}_2,\ldots,\boldsymbol{R}_n} W^{(n)}_{\boldsymbol{R}_1,\boldsymbol{R}_2,\ldots,\boldsymbol{R}_n} C_{\boldsymbol{R}_1}C_{\boldsymbol{R}_2}\ldots C_{\boldsymbol{R}_n}\right]\end{aligned} \tag{2.4}$$

where

$$\Xi_0 = \exp[-N(v_0 - \mu_{\mathrm{B}})/(k_{\mathrm{B}}T)] \tag{2.5}$$

$$W^{(n)}_{\boldsymbol{R}_1,\boldsymbol{R}_2,\ldots,\boldsymbol{R}_n} = \begin{cases} V^{(2)}_{\boldsymbol{R}_1,\boldsymbol{R}_2} + \mu\delta_{\boldsymbol{R}_1,\boldsymbol{R}_2} & \text{if } n = 2 \\ V^{(n)}_{\boldsymbol{R}_1,\boldsymbol{R}_2,\ldots,\boldsymbol{R}_n} & \text{if } n > 2 \end{cases} \tag{2.6}$$

$$\mu = 2(V^{(1)}_{\boldsymbol{R}} - \mu_{\mathrm{A}} + \mu_{\mathrm{B}}) \tag{2.7}$$

μ_{A}, N_{A} and μ_{B}, N_{B} are the chemical potentials and the total numbers of A and B-type atoms, respectively, T is the absolute temperature, k_{B} is the Boltzmann constant, the summation on $\{C_{\mathrm{R}}\}$ is carried over all possible atomic configurations and $\delta_{\boldsymbol{R}_1,\boldsymbol{R}_2}$ is the Kronecker delta. At the derivation of (2.4), the symmetry equivalence of the crystal lattice sites in the case of the disordered state of the alloy was taken into account [35, 36] and the following relationships

$$N_{\mathrm{A}} + N_{\mathrm{B}} = N \tag{2.8}$$

$$N_{\mathrm{A}} = \sum_{\boldsymbol{R}} C_{\boldsymbol{R}} \tag{2.9}$$

$$[C_{\boldsymbol{R}}]^n = C_{\boldsymbol{R}} \tag{2.10}$$

where n is a positive integer, were used.

Note that the expression (2.4) for the grand partition function can be converted into the expression for the *canonical* partition function by setting $\mu = 0$ (under neglect of the configuration-independent multiplier). This allows us, if need be, to make a step from the grand canonical ensemble to the canonical one in the expressions for configurational statistical–thermodynamic characteristics of the alloy by setting $\mu = 0$.

In the present section, we shall assume the presence of a LRO in the alloy with the purpose of the further use of the thermodynamic fluctuation method, in which the SRO is considered as fluctuations of the equilibrium LRO. In the following sections, after the application of the fluctuation method, the LRO parameters will be put equal to zero, according to the aim of the present paper to investigate just the disordered state of the alloy.

Thus, let us replace the summation over $\{C_{\boldsymbol{R}}\}$ in the partition function (2.4) by the summation over $\{C_{\boldsymbol{R}}\}_{\mathrm{LRO}}$ over all states with some given values of the LRO parameters [3, 21–24, 37–40]. The expression for the corresponding grand thermodynamic potential Ω can be presented as follows

$$\Omega = -k_{\mathrm{B}}T \ln \Xi = \Omega_0 - k_{\mathrm{B}}T \ln \Delta\Gamma + \Delta\Omega \tag{2.11}$$

where

$$\Omega_0 = -k_{\mathrm{B}}T \ln \Xi_0 = N(v_0 - \mu_{\mathrm{B}}) \tag{2.12}$$

$$\Delta\Omega = -k_{\mathrm{B}}T \ln\left\langle \exp\left[-(k_{\mathrm{B}}T)^{-1}\sum_{n=2}^{N}\frac{1}{n!}\sum_{\boldsymbol{R}_1,\boldsymbol{R}_2,\ldots,\boldsymbol{R}_n} W^{(n)}_{\boldsymbol{R}_1,\boldsymbol{R}_2,\ldots,\boldsymbol{R}_n} C_{\boldsymbol{R}_1}C_{\boldsymbol{R}_2}\ldots C_{\boldsymbol{R}_n}\right]\right\rangle \tag{2.13}$$

$$\Delta\Gamma = \sum_{\{C_{\boldsymbol{R}}\}_{\mathrm{LRO}}} 1. \tag{2.14}$$

$\Delta\Gamma$ is the number of configurations corresponding to a state with a given LRO, and (see, e.g., [39, 40])

$$\ln \Delta\Gamma = -\sum_{\boldsymbol{R}} [P_{\boldsymbol{R}} \ln P_{\boldsymbol{R}} + (1 - P_{\boldsymbol{R}}) \ln(1 - P_{\boldsymbol{R}})] \tag{2.15}$$

where the value

$$P_{\boldsymbol{R}} = \langle C_{\boldsymbol{R}} \rangle \tag{2.16}$$

is equal to the probability of finding an A-type atom at the site $\boldsymbol{R}$. In (2.13) and below, $\langle \ldots \rangle$ means the statistical average over all states with given values of the LRO parameters:

$$\langle \ldots \rangle = \Delta\Gamma^{-1} \sum_{\{C_{\boldsymbol{R}}\}_{\text{LRO}}} \ldots . \tag{2.17}$$

Notice that the values of the chemical potentials μ_{A} and μ_{B} and, therefore (see (2.7)), the value of μ must satisfy the general thermodynamic relationships [41]

$$\langle N_{\text{A}} \rangle = -(\partial\Omega/\partial\mu_{\text{A}})_T \qquad \langle N_{\text{B}} \rangle = -(\partial\Omega/\partial\mu_{\text{B}})_T . \tag{2.18}$$

3. Cumulant expansion

According to the general approach of the thermodynamic perturbation theory [18, 21–24, 37–41], we expand the expression (2.13) in a cumulant series in powers of the inverse temperature

$$\Delta\Omega = -k_{\text{B}}T \ln\left\langle \exp\left(-\frac{X}{k_{\text{B}}T}\right)\right\rangle = -k_{\text{B}}T \sum_{n=1}^{\infty} \frac{1}{n!} \frac{M_n(X)}{(-k_{\text{B}}T)^n} \tag{3.1}$$

where

$$X = \sum_{t=2}^{N} \frac{1}{t!} \sum_{\boldsymbol{R}_1,\boldsymbol{R}_2,\ldots,\boldsymbol{R}_t} W^{(f)}_{\boldsymbol{R}_1,\boldsymbol{R}_2,\ldots,\boldsymbol{R}_t} C_{\boldsymbol{R}_1} C_{\boldsymbol{R}_2} \ldots C_{\boldsymbol{R}_t} \tag{3.2}$$

and $M_n(X)$ is the cumulant of the nth order (see, e.g., equations (3.3) and (3.4) in [18]).

Let us consider the cumulant of the first order. By the same transformations as in (3.8) in [18], we obtain

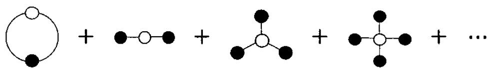
$$\begin{aligned} M_1(X) = \langle X \rangle = {} & \frac{1}{2} \sum_{\boldsymbol{R}} W^{(2)}_{\boldsymbol{R}=\boldsymbol{0}} M^0_2(\boldsymbol{R}) \\ & + \sum_{t=2}^{N} \frac{1}{t!} \sum_{\boldsymbol{R}_1,\boldsymbol{R}_2,\ldots,\boldsymbol{R}_t} W^{(t)}_{\boldsymbol{R}_1,\boldsymbol{R}_2,\ldots,\boldsymbol{R}_t} M^0_1(\boldsymbol{R}_1) M^0_1(\boldsymbol{R}_2) \ldots M^0_1(\boldsymbol{R}_t) \end{aligned} \tag{3.3}$$

where

$$M^0_1(\boldsymbol{R}) = P_{\boldsymbol{R}} \qquad M^0_2(\boldsymbol{R}) = P_{\boldsymbol{R}}(1 - P_{\boldsymbol{R}}). \tag{3.4}$$

The expression (3.3) can be written down in the following diagram form

$$M_1(X) =$$



(3.5)

to match up both the summation $\sum_{\boldsymbol{R}_i}$ and the multiplier $M^0_{l_i}(\boldsymbol{R}_i)$ to each solid vertex $\boldsymbol{R}_i$ with l_i lines entering it, as well as to match up the open vertex with t lines beginning in it and finishing in solid vertexes $\boldsymbol{R}_1, \boldsymbol{R}_2, \ldots, \boldsymbol{R}_t$ to the mixing potential $W^{(t)}_{\boldsymbol{R}_1,\boldsymbol{R}_2,\ldots,\boldsymbol{R}_t}$.

To develop the diagram technique for the cumulant expansion (3.1), let us consider the cumulant $M_n(X)$ of any given order n. In the expression for such a cumulant, the term $\langle X^n\rangle$ is always present [18]. This term can be written in the following form

$$\begin{aligned}\langle X^n\rangle &= \left\langle\left(\sum_{t=2}^{N}\frac{1}{t!}\sum_{\boldsymbol{R}_1,\boldsymbol{R}_2,\dots,\boldsymbol{R}_t} W^{(t)}_{\boldsymbol{R}_1,\boldsymbol{R}_2,\dots,\boldsymbol{R}_t} C_{\boldsymbol{R}_1}C_{\boldsymbol{R}_2}\dots C_{\boldsymbol{R}_t}\right)^n\right\rangle\\ &= \left\langle\left(\frac{1}{2}\sum_{i=1}^{N} W^{(2)}_{\boldsymbol{R}=\boldsymbol{0}}C_{\boldsymbol{R}_i} + \sum_{t=2}^{N}\sum_{i_1>i_2>\dots>i_t=1}^{N} W^{(t)}_{\boldsymbol{R}_{i_1},\boldsymbol{R}_{i_2},\dots,\boldsymbol{R}_{i_t}} C_{\boldsymbol{R}_{i_1}}C_{\boldsymbol{R}_{i_2}}\dots C_{\boldsymbol{R}_{i_t}}\right)^n\right\rangle\end{aligned} \tag{3.6}$$

where the summations are carried over all sites of the crystal lattice numbered by $1, 2, \dots, N$. Let us transform (3.6) as follows

$$\begin{aligned}\langle X^n\rangle = n! \sum_{\substack{\{m^{(1)}_{i_1}=0\}\\ (\sum_{t=1}^{N}\sum_{i_1>i_2>\dots>i_t=1} m^{(t)}_{i_1 i_2\dots i_t}=n)}}^{n} \sum_{\{m^{(2)}_{i_1 i_2}\}=0}^{n}\dots\sum_{\{m^{(N)}_{i_1 i_2\dots i_N}\}=0}^{n} \left\langle \prod_{i=1}^{N}\left[\frac{(\frac{1}{2}W^{(2)}_{\boldsymbol{R}=\boldsymbol{0}}C_{\boldsymbol{R}_i})^{m^{(1)}_{i_1}}}{m^{(1)}_{i_1}!}\right]\right.\\ \left.\times\prod_{t=2}^{N}\prod_{i_1>i_2>\dots>i_t=1}^{N}\left[\frac{(W^{(t)}_{\boldsymbol{R}_{i_1},\boldsymbol{R}_{i_2},\dots,\boldsymbol{R}_{i_t}}C_{\boldsymbol{R}_{i_1}}C_{\boldsymbol{R}_{i_2}}\dots C_{\boldsymbol{R}_{i_t}})^{m^{(t)}_{i_1 i_2\dots i_t}}}{m^{(t)}_{i_1 i_2\dots i_t}!}\right]\right\rangle.\end{aligned} \tag{3.7}$$

In analogy with $M_1(x)$ (see (3.3)–(3.5)), a diagram consisting of open and solid vertexes linked by lines can be put into correspondence to each term in (3.7). So, grouping together the terms that correspond to topologically equivalent diagrams, we obtain

$$\begin{aligned}\langle X^n\rangle = n! \sum_{\substack{\text{diagram}\\ (\sum_{t=1}^{N}\sum_{i_1>i_2>\dots>i_t=1}^{N} m^{(t)}_{i_1 i_2\dots i_t}=n)}} \frac{S}{p!}\sum_{\boldsymbol{R}_1\neq\boldsymbol{R}_2\neq\dots\neq\boldsymbol{R}_p}\prod_{i=1}^{p}\left[\frac{(\frac{1}{2}W^{(2)}_{\boldsymbol{R}=\boldsymbol{0}})^{m^{(1)}_i}}{m^{(1)}_i!}\right]\\ \times\prod_{t=2}^{p}\prod_{i_1>i_2>\dots>i_t=1}^{p}\left[\frac{(W^{(t)}_{\boldsymbol{R}_{i_1},\boldsymbol{R}_{i_2},\dots,\boldsymbol{R}_{i_t}})^{m^{(t)}_{i_1 i_2\dots i_t}}}{m^{(t)}_{i_1 i_2\dots i_t}!}\right]\left\langle\prod_{j=1}^{p}(C_{\boldsymbol{R}_j})^{l_j}\right\rangle.\end{aligned} \tag{3.8}$$

where $\sum_{\text{diagram}}$ means the summation over all topologically unequivalent diagrams; the solid vertices of a diagram are numbered by $1, 2, \dots, p$; the summations on the vectors $\boldsymbol{R}_1, \boldsymbol{R}_2, \dots, \boldsymbol{R}_p$ are carried over all N crystal lattice sites;

$$S = \frac{p!}{t} \tag{3.9}$$

is the number of nonequivalent ways of distribution of p unequal fixed indices through the p solid vertices of a given diagram (t is the number of elements of the topological symmetry group of a diagram); $m^{(1)}_i$ is the number of 'loops' corresponding to the ith solid vertex (i.e. the number of open vertices each with two lines beginning in it and finished in the same ith solid vertex); $m^{(t)}_{i_1 i_2\dots i_t}$ ($t > 2$) is the number of open vertices each with t lines beginning in it and finished in the same $i_1, i_2, \dots, i_t$ solid different vertices; l_i is the total number of lines entering the ith solid vertex. Note that there does not exist an open vertex with $t > 2$ lines beginning in it, any two lines of which are finished in the same solid vertex (see (2.3) and (2.6)).

Horwitz and Callen [42] proved that the transition in consideration

$$\langle X^n\rangle \to M_n(X)$$

is equivalent (in our designations) to the simultaneous performance of the two following changes

$$\left\langle \prod_{j=1}^{p} (C_{\boldsymbol{R}_j})^{l_j} \right\rangle \to \prod_{j=1}^{p} M^0_{l_j}(\boldsymbol{R}_j) \qquad \sum_{\boldsymbol{R}_1 \neq \boldsymbol{R}_2 \neq \cdots \neq \boldsymbol{R}_p} \to \sum_{\boldsymbol{R}_1, \boldsymbol{R}_2, \ldots, \boldsymbol{R}_p}$$

where

$$M^0_{l_i}(\boldsymbol{R}_i) = M_{l_i}(C_{\boldsymbol{R}_i}) \tag{3.10}$$

taking into account only linked diagrams, i.e. those which do not consist of several isolated parts. Performing these changes in (3.8), we obtain

$$\frac{M_n(X)}{n!(-k_{\mathrm{B}}T)^{n-1}} = \sum_{\substack{\text{diagram} \\ (\sum_{t=1}^{N} \sum_{i_1 > i_2 > \cdots > i_t = 1}^{N} m^{(t)}_{i_1 i_2 \ldots i_t = n})}} \frac{S}{p!(-k_{\mathrm{B}}T)^{n-1}} \sum_{\boldsymbol{R}_1, \boldsymbol{R}_2, \ldots, \boldsymbol{R}_p}$$
$$\times \prod_{i=1}^{p} \left[\frac{(\frac{1}{2} W^{(2)}_{\boldsymbol{R}=\boldsymbol{0}})^{m^{(1)}_i} M^0_{l_i}(\boldsymbol{R}_i)}{m^{(1)}_i!} \right] \prod_{t=2}^{p} \prod_{i_1 > i_2 > \cdots > i_t = 1}^{p} \left[\frac{(W^{(t)}_{\boldsymbol{R}_{i_1}, \boldsymbol{R}_{i_2}, \ldots, \boldsymbol{R}_{i_t}})^{m^{(t)}_{i_1 i_2 \ldots i_t}}}{m^{(t)}_{i_1 i_2 \ldots i_t}!} \right]. \tag{3.11}$$

From (3.11), it follows that to each term that contributes to the cumulant series (3.1) one can assign a linked diagram consisting of open vertices with lines beginning in it and finished in solid vertices, if one used the following diagram technique rules:

(1) to match up the multiplier

$$\frac{(W^{(t)}_{\boldsymbol{R}_{i_1}, \boldsymbol{R}_{i_2}, \ldots, \boldsymbol{R}_{i_t}})^{m^{(t)}_{i_1 i_2 \ldots i_t}}}{m^{(t)}_{i_1 i_2 \ldots i_t}!}$$

to all $m^{(t)}_{i_1 i_2 \ldots i_t}$ *open* vertices each with t lines beginning in it and finishing in the same $i_1, i_2, \ldots, i_t$ solid *different* vertices;

(2) to match up the summation $\sum_{\boldsymbol{R}_i}$ and the multiplier

$$\frac{(W^{(2)}_{\boldsymbol{R}=\boldsymbol{0}}/2)^{m^{(1)}_i} M^0_{l_i}(\boldsymbol{R}_i)}{m^{(1)}_i!}$$

to each *solid* vertex $\boldsymbol{R}_i$ with l_i lines entering it and $m^{(1)}_i$ 'loops' (see above) corresponding to it;

(3) to multiply the expression obtained in the previous steps by a combinatorial factor

$$\frac{S}{p!(-k_{\mathrm{B}}T)^{n-1}} \tag{3.12}$$

where n and p are the total numbers of open and solid vertices in a diagram, respectively, and the quantity S is determined in (3.9).

4. High-temperature approximation

It is evident that at sufficiently high temperatures, the terms that are proportional to the least powers of $(k_{\mathrm{B}}T)^{-1}$ mainly contribute to the cumulant expansion (3.1). Taking into account only the terms proportional to the zero power of $(k_BT)^{-1}$ in (3.1) and using (3.3), we obtain in the corresponding high-temperature (HT) approximation

$$\Delta\Omega_{\mathrm{HT}} = M_1(X) = \frac{1}{2}Nc\mu + \sum_{t=2}^{N}\frac{1}{t!}\sum_{\boldsymbol{R}_1,\boldsymbol{R}_2,\ldots,\boldsymbol{R}_t} V^{(t)}_{\boldsymbol{R}_1,\boldsymbol{R}_2,\ldots,\boldsymbol{R}_t} P_{\boldsymbol{R}_1}P_{\boldsymbol{R}_2}\ldots P_{\boldsymbol{R}_t} \tag{4.1}$$

where c is the concentration of A-type atoms in the alloy

$$c = \frac{\langle N_{\mathrm{A}}\rangle}{N}. \tag{4.2}$$

Note that, in classification of the cumulant expansion terms by the powers of $(k_BT)^{-1}$, we neglect the temperature dependence of the quantity μ entering the cumulant expansion through the function $W^{(2)}_{\boldsymbol{R}_1,\boldsymbol{R}_2}$ (see (2.6)). Substituting (4.1) into (2.11), we have the following expression for the corresponding grand thermodynamic potential Ω_{HT}

$$\Omega_{\mathrm{HT}} = \Omega^{(0)}_{\mathrm{HT}} + \sum_{t=2}^{N}\frac{1}{t!}\sum_{\boldsymbol{R}_1,\boldsymbol{R}_2,\ldots,\boldsymbol{R}_t} V^{(t)}_{\boldsymbol{R}_1,\boldsymbol{R}_2,\ldots,\boldsymbol{R}_t} P_{\boldsymbol{R}_1}P_{\boldsymbol{R}_2}\ldots P_{\boldsymbol{R}_t} - k_BT\ln\Delta\Gamma \tag{4.3}$$

where

$$\Omega^{(0)}_{\mathrm{HT}} = \Omega_0 + \tfrac{1}{2}Nc\mu. \tag{4.4}$$

It should be noted that the obtained expression for the grand thermodynamic potential corresponds to that of the free energy derived in [1] (equations (2.4)–(2.6)) within the mean-field approximation.

In the case of the disordered state of the alloy, when for any $\boldsymbol{R}$

$$P_{\boldsymbol{R}} = c \tag{4.5}$$

the expression (4.3) takes the following form

$$\Omega_{\mathrm{HT}}|_{P_{\boldsymbol{R}}=c} = \Omega^{(0)}_{\mathrm{HT}} + N\left\{\sum_{t=2}^{N}\frac{c^t}{t!}\tilde{V}^{(t)}_{\boldsymbol{0},\boldsymbol{0},\ldots,\boldsymbol{0}} + k_BT[c\ln c + (1-c)\ln(1-c)]\right\} \tag{4.6}$$

where we introduced the Fourier transforms $\tilde{V}^{(t)}_{\boldsymbol{k}_1,\boldsymbol{k}_2,\ldots,\boldsymbol{k}_{t-1}}$ of the mixing potentials determined as [1, 35, 36]:

$$\tilde{V}^{(t)}_{\boldsymbol{k}_1,\boldsymbol{k}_2,\ldots,\boldsymbol{k}_{t-1}} = \sum_{\boldsymbol{R}_1,\boldsymbol{R}_2,\ldots,\boldsymbol{R}_{t-1}} V^{(t)}_{\boldsymbol{R}_1,\boldsymbol{R}_2,\ldots,\boldsymbol{R}_{t-1},\boldsymbol{0}} \exp\left(-\mathrm{i}\sum_{l=1}^{t-1}\boldsymbol{k}_l\boldsymbol{R}_l\right) \tag{4.7a}$$

$$V^{(t)}_{\boldsymbol{R}_1,\boldsymbol{R}_2,\ldots,\boldsymbol{R}_t} = \frac{1}{N^{t-1}}\sum_{\boldsymbol{k}_1,\boldsymbol{k}_2,\ldots,\boldsymbol{k}_{t-1}} \tilde{V}^{(t)}_{\boldsymbol{k}_1,\boldsymbol{k}_2,\ldots,\boldsymbol{k}_{t-1}} \exp\left[-\mathrm{i}\sum_{l=1}^{t-1}\boldsymbol{k}_l(\boldsymbol{R}_l-\boldsymbol{R}_n)\right]. \tag{4.7b}$$

In (4.7*b*) and below, the summations over the wave vectors are carried out over all the points specified by the cyclic boundary conditions in the corresponding first Brillouin zone.

In the present paper, for calculation of the Warren–Cowley SRO parameters $\alpha_{\boldsymbol{R}}$ determined [43, 44] as the two-body correlation function divided by $c(1-c)$:

$$\alpha_{\boldsymbol{R}_1-\boldsymbol{R}_2} = \frac{\langle C_{\boldsymbol{R}_1}C_{\boldsymbol{R}_2}\rangle - c^2}{c(1-c)} \tag{4.8}$$

as well as for calculation of the Fourier transform $\alpha_{\boldsymbol{k}}$ of these parameters:

$$\alpha_{\boldsymbol{k}} = \sum_{\boldsymbol{R}}\alpha_{\boldsymbol{R}}\exp(-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{R}) \qquad \alpha_{\boldsymbol{R}} = N^{-1}\sum_{\boldsymbol{q}}\alpha_{\boldsymbol{q}}\exp(\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{R}) \tag{4.9}$$

we use the thermodynamic fluctuation method [2–5, 39–41], whose high accuracy was demonstrated in [1, 18, 19]. Applying this method within the high-temperature approximation (4.3), we obtain

$$\alpha_{\boldsymbol{k}} = 1 - N^{-1} \sum_{\boldsymbol{q}} \beta_{\boldsymbol{q}}^{\mathrm{HT}} + \beta_{\boldsymbol{k}}^{\mathrm{HT}} \tag{4.10}$$

where

$$\beta_{\boldsymbol{k}}^{\mathrm{HT}} = \left[1 + \frac{c(1-c)}{k_{\mathrm{B}}T} \tilde{V}_{\boldsymbol{k}}^{\mathrm{eff}}\right]^{-1} \tag{4.11}$$

$$\tilde{V}_{\boldsymbol{k}}^{\mathrm{eff}} = \sum_{m=0}^{N-2} \frac{c^m}{m!} \tilde{V}_{\boldsymbol{k},\boldsymbol{0},\boldsymbol{0},\ldots,\boldsymbol{0}}^{(2+m)} = \tilde{V}_{\boldsymbol{k}}^{(2)} + c\tilde{V}_{\boldsymbol{k},\boldsymbol{0}}^{(3)} + \frac{c^2}{2} \tilde{V}_{\boldsymbol{k},\boldsymbol{0},\boldsymbol{0}}^{(4)} + \cdots. \tag{4.12}$$

The obtained expression (4.10) (taking into account (4.11) and (4.12)) coincides with the expression (2.22) in [1].

5. Generalized Brout classification

Brout [21–24] offered a method for estimation of the contribution from every diagram in the cumulant expansion by the power of the quantity z^{-1}, where z is the effective number of atoms interacting with one fixed atom. Generalizing such an approach to the case of the presence of many-body atomic interactions of arbitrary orders in an alloy, we have

$$k_{\mathrm{B}}T \propto z^{t-1} V^{(t)} \Rightarrow \frac{V^{(t)}}{k_{\mathrm{B}}T} \propto [z^{-1}]^{t-1} \tag{5.1}$$

where $V^{(t)}$ is an effective parameter that characterizes the t-body ($t = 2, 3, \ldots$) atomic interactions in the alloy. In (5.1), the competition between the entropy ($k_{\mathrm{B}}T$) and energy ($z^{t-1}V^{(t)}$) contributions to the thermodynamic potential near the temperature of the order–disorder phase transition is taken into account. Using (5.1) as well as the following estimation [21, 22, 24, 45]

$$\sum_{\boldsymbol{R}_1, \boldsymbol{R}_2, \ldots, \boldsymbol{R}_p} \propto N[z^{-1}]^{1-p} \tag{5.2}$$

and putting into correspondence the multiplier $V^{(t)}/(k_{\mathrm{B}}T)$ with every open vertex with t lines beginning in it and the summation $\sum_{\boldsymbol{R}}$ with every solid vertex of a diagram, the relative contribution from a diagram with n open and p solid vertices to the cumulant expansion (3.1) may be estimated by the value

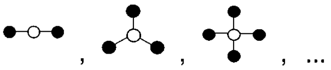
$$N[z^{-1}]^{\sum_i (l_i - 1) + 1 - p} = N[z^{-1}]^{\sum_i (l_i) - n + 1 - p}. \tag{5.3}$$

In (5.3) the summation $\sum_i$ is carried over all open vertices of a diagram and t_i is the number of lines beginning in the ith vertex.

At a sufficiently large value of the effective radius of atomic interactions (i.e. at large value of z), one may suppose quick convergence in the framework of the perturbation theory based on a choice of the quantity z^{-1} as a small parameter of expansion. In the next two sections, the two lowest orders (zeroth and first) of such a perturbation theory will be considered. Note that, in the cumulant expansion, we shall not take into account the comparatively small (as proved by Brout [18, 19, 21]) contribution from the reducible diagrams, each of which, by definition, can be transformed into an unlinked diagram by cutting in some vertex.

6. Generalized zero approximation

By use of (5.3), one may conclude that the contribution from only such linked irreducible diagrams as



(6.1)

is proportional to the least, zeroth power of the quantity z^{-1}. Each such diagram consists of one open vertex with t lines ($t = 2, 3, \ldots$) beginning in it and finishing in t solid vertices. Let us call the approximation in which the contribution from only such diagrams is taken into account in (3.1) the generalized zero approximation. Within such an approximation, the expression for the grand thermodynamic potential is the following

$$\Omega_{\mathrm{zero}} = \Omega_0 + \sum_{t=2}^{N} \frac{1}{t!} \sum_{\boldsymbol{R}_1,\boldsymbol{R}_2,\ldots,\boldsymbol{R}_t} W^{(t)}_{\boldsymbol{R}_1,\boldsymbol{R}_2,\ldots,\boldsymbol{R}_t} P_{\boldsymbol{R}_1} P_{\boldsymbol{R}_2} \ldots P_{\boldsymbol{R}_t} - k_{\mathrm{B}} T \ln \Delta\Gamma. \tag{6.2}$$

In the case of the disordered state of the alloy, the expression (6.2) takes the following form (see (2.6), (4.5), (4.7))

$$\Omega_{\mathrm{zero}}|_{P_{\boldsymbol{R}}=c} = \Omega_0 + N\left\{\frac{1}{2}\mu c^2 + \sum_{t=2}^{N} \frac{c^t}{t!} \tilde{V}^{(t)}_{\boldsymbol{0},\boldsymbol{0},\ldots,\boldsymbol{0}} + k_{\mathrm{B}} T[c \ln c + (1-c)\ln(1-c)]\right\}. \tag{6.3}$$

Applying the thermodynamic fluctuation method within the generalized zero approximation, we obtain

$$\alpha_{\boldsymbol{k}} = \left[1 + \frac{c(1-c)}{k_{\mathrm{B}} T}(\mu + \tilde{V}^{\mathrm{eff}}_{\boldsymbol{k}})\right]^{-1} \tag{6.4}$$

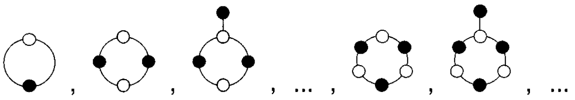
where the quantity μ should be found from the following equation

$$N^{-1} \sum_{\boldsymbol{q}} \alpha_{\boldsymbol{q}} = 1. \tag{6.5}$$

The expressions (6.4) and (6.5) correspond to the generalized (to the case of taking into account many-body atomic interactions of arbitrary orders) spherical model approximation (see (2.24) and (2.25) in [1]).

7. Generalized ring approximation

According to the estimation (5.3), the contributions from the terms corresponding to the following linked irreducible diagrams of the generalized ring type



(7.1)

are proportional to the first power of the quantity z^{-1}. In each such diagram an arbitrary number of open vertices of arbitrary orders form a ring. Two lines (per open vertex) among all lines beginning in open vertices are used to form a ring, whereas the other such lines finish in solid vertices isolated from a ring. By use of the diagram technique rules described in section 3, let us separate out the contribution $\Delta\Omega_{\mathrm{ring}}$ corresponding to such diagrams in the expansion (3.1):

$$\Delta\Omega_{\mathrm{ring}} = -\frac{k_{\mathrm{B}} T}{2} \sum_{n=1}^{\infty} [n(-k_{\mathrm{B}} T)^n]^{-1} \sum_{\boldsymbol{R}_1,\boldsymbol{R}_2,\ldots,\boldsymbol{R}_n} f_{\boldsymbol{R}_1-\boldsymbol{R}_2} f_{\boldsymbol{R}_2-\boldsymbol{R}_3} \cdots f_{\boldsymbol{R}_n-\boldsymbol{R}_1} \tag{7.2}$$

where

$$f_{\boldsymbol{R}_i-\boldsymbol{R}_j} = P_{\boldsymbol{R}_i}(1-P_{\boldsymbol{R}_i})\sum_{l=0}^{N-2}\sum_{\boldsymbol{R}'_1,\boldsymbol{R}'_2,\ldots,\boldsymbol{R}'_l}\frac{P_{\boldsymbol{R}'_1}P_{\boldsymbol{R}'_2}\ldots P_{\boldsymbol{R}'_l}}{l!}W^{(2+l)}_{\boldsymbol{R}_i,\boldsymbol{R}_j,\boldsymbol{R}'_1,\boldsymbol{R}'_2,\ldots,\boldsymbol{R}'_l}. \tag{7.3}$$

Taking into account the contributions corresponding to the diagrams (6.1) and (7.1) in the cumulant expansion, we have the following form for the corresponding grand thermodynamic potential:

$$\Omega_{\mathrm{ring}} = \Omega_{\mathrm{zero}} + \Delta\Omega_{\mathrm{ring}} \tag{7.4}$$

where Ω_{zero} and $\Delta\Omega_{\mathrm{ring}}$ are determined by the expressions (6.2) and (7.2), respectively. We shall call this approximation the generalized ring one. In the case of the disordered state of the alloy (see (4.5)), the expression (7.2) can be transformed as follows

$$\Delta\Omega_{\mathrm{ring}}|_{P_{\boldsymbol{R}}=c} = \frac{k_{\mathrm{B}}T}{2}\sum_{\boldsymbol{q}}\ln\left[1+\frac{c(1-c)}{k_{\mathrm{B}}T}(\mu+\tilde{V}^{\mathrm{eff}}_{\boldsymbol{q}})\right]. \tag{7.5}$$

Applying the thermodynamic fluctuation method within the generalized ring approximation, we obtain

$$\alpha_{\boldsymbol{k}} = \left[1+\frac{c(1-c)}{k_{\mathrm{B}}T}(\mu+\tilde{V}^{\mathrm{eff}}_{\boldsymbol{k}}+\tilde{V}^{\mathrm{ring}}_{\boldsymbol{k}})\right]^{-1} \tag{7.6}$$

where

$$\tilde{V}^{\mathrm{ring}}_{\boldsymbol{k}} = \frac{1}{N}\sum_{\boldsymbol{q}}\left\{\frac{c(1-c)\phi^{(4)}_{\boldsymbol{q},\boldsymbol{k},-\boldsymbol{k}}/2+(1-2c)\phi^{(3)}_{\boldsymbol{q},\boldsymbol{k}-\boldsymbol{q}}-\phi^{(2)}_{\boldsymbol{q}}}{1+\phi^{(2)}_{\boldsymbol{q}}c(1-c)/(k_{\mathrm{B}}T)}\right.$$
$$\left.-\frac{[c(1-c)\phi^{(3)}_{\boldsymbol{q},\boldsymbol{k}-\boldsymbol{q}}]^2+2c(1-c)(1-2c)\phi^{(2)}_{\boldsymbol{q}}\phi^{(3)}_{\boldsymbol{q},\boldsymbol{k}-\boldsymbol{q}}+(1-2c)^2\phi^{(2)}_{\boldsymbol{q}}\phi^{(2)}_{\boldsymbol{k}-\boldsymbol{q}}}{2k_{\mathrm{B}}T[1+\phi^{(2)}_{\boldsymbol{q}}c(1-c)/(k_{\mathrm{B}}T)][1+\phi^{(2)}_{\boldsymbol{k}-\boldsymbol{q}}c(1-c)/(k_{\mathrm{B}}T)]}\right\} \tag{7.7}$$

$$\phi^{(n)}_{\boldsymbol{k}_1,\boldsymbol{k}_2,\ldots,\boldsymbol{k}_{n-1}} = \mu\delta_{n,2}+\tilde{\Phi}^{(n)}_{\boldsymbol{k}_1,\boldsymbol{k}_2,\ldots,\boldsymbol{k}_{n-1}} \tag{7.8}$$

$$\tilde{\Phi}^{(n)}_{\boldsymbol{k}_1,\boldsymbol{k}_2,\ldots,\boldsymbol{k}_{n-1}} = \sum_{l=0}^{N-n}\frac{c^l}{l!}\tilde{V}^{(n+l)}_{\boldsymbol{k}_1,\boldsymbol{k}_2,\ldots,\boldsymbol{k}_{n-1},\mathbf{0},\mathbf{0},\ldots,\mathbf{0}} = V^{(n)}_{\boldsymbol{k}_1,\boldsymbol{k}_2,\ldots,\boldsymbol{k}_{n-1}}$$
$$+cV^{(n+1)}_{\boldsymbol{k}_1,\boldsymbol{k}_2,\ldots,\boldsymbol{k}_{n-1},\mathbf{0}}+c^2/2V^{(n+2)}_{\boldsymbol{k}_1,\boldsymbol{k}_2,\ldots,\boldsymbol{k}_{n-1},\mathbf{0},\mathbf{0}}+\cdots \tag{7.9}$$

$(n = 0, 1, \ldots)$ and the quantity μ should be found from the following equation

$$N^{-1}\sum_{\boldsymbol{q}}\alpha_{\boldsymbol{q}} = 1. \tag{7.10}$$

Note that (see (4.12), (7.8), (7.9))

$$\phi^{(2)}_{\boldsymbol{k}} = \mu+\tilde{\Phi}^{(2)}_{\boldsymbol{k}} = \mu+\tilde{V}^{\mathrm{eff}}_{\boldsymbol{k}}. \tag{7.11}$$

From comparison of (6.4) with (7.6), it follows that the difference between the generalized spherical model and ring approximations consists in the presence of the quantity $\tilde{V}^{\mathrm{ring}}_{\boldsymbol{k}}$, which is temperature and concentration dependent. It easy also to verify that neglecting the nonpair atomic interactions, when

$$\phi^{(2)}_{\boldsymbol{k}} \to \mu+\tilde{V}^{(2)}_{\boldsymbol{k}} \qquad \phi^{(3)}_{\boldsymbol{k}_1,\boldsymbol{k}_2} \to 0 \qquad \phi^{(4)}_{\boldsymbol{k}_1,\boldsymbol{k}_2,\boldsymbol{k}_3} \to 0 \tag{7.12}$$

the expressions (7.6) and (7.7) transform into the corresponding expressions obtained in [18] within the ring approximation.

With the aim of practical use, let us write down the expressions for the functions $\phi^{(n)}_{\boldsymbol{k}_1,\boldsymbol{k}_2,\ldots,\boldsymbol{k}_{n-1}}$ with $n = 2, 3, 4$ (appearing in the expression (7.7) for $\tilde{V}^{\text{ring}}_{\boldsymbol{k}}$) in terms of the Fourier transforms $V^{(n)}_{\boldsymbol{k}_1,\boldsymbol{k}_2,\ldots,\boldsymbol{k}_{n-1}}$ taking into account only pair, triplet and quadruplet atomic interactions:

$$\phi^{(2)}_{\boldsymbol{k}} = \mu + \tilde{\Phi}^{(2)}_{\boldsymbol{k}} = \mu + V^{(2)}_{\boldsymbol{k}} + cV^{(3)}_{\boldsymbol{k},\boldsymbol{0}} + c^2/2V^{(4)}_{\boldsymbol{k},\boldsymbol{0},\boldsymbol{0}} \tag{7.13}$$

$$\phi^{(3)}_{\boldsymbol{k}_1,\boldsymbol{k}_2} = \tilde{\Phi}^{(3)}_{\boldsymbol{k}_1,\boldsymbol{k}_2} = V^{(3)}_{\boldsymbol{k}_1,\boldsymbol{k}_2} + cV^{(4)}_{\boldsymbol{k}_1,\boldsymbol{k}_2,\boldsymbol{0}} \tag{7.14}$$

$$\phi^{(4)}_{\boldsymbol{k}_1,\boldsymbol{k}_2,\boldsymbol{k}_3} = \tilde{\Phi}^{(4)}_{\boldsymbol{k}_1,\boldsymbol{k}_2,\boldsymbol{k}_3} = V^{(4)}_{\boldsymbol{k}_1,\boldsymbol{k}_2,\boldsymbol{k}_3}. \tag{7.15}$$

8. Calculation of interatomic potentials

Let us describe the details of application of the generalized spherical model and ring approximations in combination with three widely used approaches for calculation of interatomic potentials in alloys.

8.1. Generalized perturbation method

Within this method [25–28], the following form, alternative to the expression (2.1), for the Hamiltonian of the system under consideration is used:

$$\begin{aligned} H &= \Phi^{(0)} + \sum_{n=1}^{N} \frac{1}{n!} \sum_{\boldsymbol{R}_1,\boldsymbol{R}_2,\ldots,\boldsymbol{R}_n} \Phi^{(n)}_{\boldsymbol{R}_1,\boldsymbol{R}_2,\ldots,\boldsymbol{R}_n} \Delta_{\boldsymbol{R}_1}\Delta_{\boldsymbol{R}_2}\ldots\Delta_{\boldsymbol{R}_n} \\ &= \Phi^{(0)} + \sum_{\boldsymbol{R}} \Phi^{(1)}_{\boldsymbol{R}}\Delta_{\boldsymbol{R}} + \frac{1}{2}\sum_{\boldsymbol{R}_1,\boldsymbol{R}_2} \Phi^{(2)}_{\boldsymbol{R}_1,\boldsymbol{R}_2}\Delta_{\boldsymbol{R}_1}\Delta_{\boldsymbol{R}_2} \\ &\quad + \frac{1}{6}\sum_{\boldsymbol{R}_1,\boldsymbol{R}_2,\boldsymbol{R}_3} \Phi^{(3)}_{\boldsymbol{R}_1,\boldsymbol{R}_2,\boldsymbol{R}_3}\Delta_{\boldsymbol{R}_1}\Delta_{\boldsymbol{R}_2}\Delta_{\boldsymbol{R}_3} + \cdots \end{aligned} \tag{8.1}$$

where [1]

$$\begin{aligned} \Phi^{(n)}_{\boldsymbol{R}_1,\boldsymbol{R}_2,\ldots,\boldsymbol{R}_n} &= \sum_{m=0}^{N-n} \frac{c^m}{m!} \sum_{\boldsymbol{R}'_1,\boldsymbol{R}'_2,\ldots,\boldsymbol{R}'_m} V^{(n+m)}_{\boldsymbol{R}_1,\boldsymbol{R}_2,\ldots,\boldsymbol{R}_n,\boldsymbol{R}'_1,\boldsymbol{R}'_2,\ldots,\boldsymbol{R}'_m} \\ &= V^{(n)}_{\boldsymbol{R}_1,\boldsymbol{R}_2,\ldots,\boldsymbol{R}_n} + c\sum_{\boldsymbol{R}'_1} V^{(n+1)}_{\boldsymbol{R}_1,\boldsymbol{R}_2,\ldots,\boldsymbol{R}_n,\boldsymbol{R}'_1} + \frac{c^2}{2}\sum_{\boldsymbol{R}'_1,\boldsymbol{R}'_2} V^{(n+2)}_{\boldsymbol{R}_1,\boldsymbol{R}_2,\ldots,\boldsymbol{R}_n,\boldsymbol{R}'_1,\boldsymbol{R}'_2} + \cdots \end{aligned} \tag{8.2}$$

$$\Delta_{\boldsymbol{R}} = C_{\boldsymbol{R}} - c. \tag{8.3}$$

The potentials $\Phi^{(n)}_{\boldsymbol{R}_1,\boldsymbol{R}_2,\ldots,\boldsymbol{R}_n}$ are just those that are calculated within the generalized perturbation method. As follows from comparison (B.6) in [1] and (7.9), the functions $\tilde{\Phi}^{(n)}_{\boldsymbol{k}_1,\boldsymbol{k}_2,\ldots,\boldsymbol{k}_{n-1}}$ appearing in the corresponding expressions (6.4) and (6.5) and (7.6)–(7.10) for the generalized spherical model and ring approximations are the Fourier transforms of the potentials $\Phi^{(n)}_{\boldsymbol{R}_1,\boldsymbol{R}_2,\ldots,\boldsymbol{R}_n}$ (8.2):

$$\tilde{\Phi}^{(n)}_{\boldsymbol{k}_1,\boldsymbol{k}_2,\ldots,\boldsymbol{k}_{n-1}} = \sum_{\boldsymbol{R}_1,\boldsymbol{R}_2,\ldots,\boldsymbol{R}_{n-1}} \Phi^{(n)}_{\boldsymbol{R}_1,\boldsymbol{R}_2,\ldots,\boldsymbol{R}_{n-1},\boldsymbol{0}} \exp\left(-\mathrm{i}\sum_{l=1}^{n-1} \boldsymbol{k}_l \cdot \boldsymbol{R}_l\right). \tag{8.4}$$

Thus, the results obtained by the generalized perturbation method can be directly used for calculation of the SRO in alloys within the generalized spherical model and ring approximations.

8.2. Mean-field concentration functional theory

Within this theory [31–33], the following functional

$$\begin{aligned}\varphi^{(0)}(\{P_{\boldsymbol{R}}\}) &= V^{(0)} + \sum_{n=1}^{N}\frac{1}{n!}\sum_{\boldsymbol{R}_1,\boldsymbol{R}_2,\ldots,\boldsymbol{R}_n} V^{(n)}_{\boldsymbol{R}_1,\boldsymbol{R}_2,\ldots,\boldsymbol{R}_n} P_{\boldsymbol{R}_1}P_{\boldsymbol{R}_2}\ldots P_{\boldsymbol{R}_n}\\ &= V^{(0)} + \sum_{\boldsymbol{R}} V^{(1)}_{\boldsymbol{R}} P_{\boldsymbol{R}} + \frac{1}{2}\sum_{\boldsymbol{R}_1,\boldsymbol{R}_2} V^{(2)}_{\boldsymbol{R}_1,\boldsymbol{R}_2} P_{\boldsymbol{R}_1}P_{\boldsymbol{R}_2}\\ &\quad + \frac{1}{6}\sum_{\boldsymbol{R}_1,\boldsymbol{R}_2,\boldsymbol{R}_3} V^{(3)}_{\boldsymbol{R}_1,\boldsymbol{R}_2,\boldsymbol{R}_3} P_{\boldsymbol{R}_1}P_{\boldsymbol{R}_2}P_{\boldsymbol{R}_3} + \cdots \end{aligned} \tag{8.5}$$

is calculated, where

$$V^{(0)} = Nv_0. \tag{8.6}$$

The functional (8.5) is in fact the mean-field approximation for the energy of the alloy (compare (8.5) with (2.5) in [1]). In the case of the disordered state of the alloy (see (4.5) and (8.2))

$$\varphi^{(0)}(\{P_{\boldsymbol{R}}\})|_{P_{\boldsymbol{R}}=c} = \Phi^{(0)}. \tag{8.7}$$

In analogy with (8.5), let us define the following generalized functionals ($n = 0, 1, \ldots$)

$$\begin{aligned}\varphi^{(n)}_{\boldsymbol{R}_1,\boldsymbol{R}_2,\ldots,\boldsymbol{R}_n}(\{P_{\boldsymbol{R}}\}) &= \sum_{m=0}^{N-n}\frac{1}{m!}\sum_{\boldsymbol{R}'_1,\boldsymbol{R}'_2,\ldots,\boldsymbol{R}'_m} V^{(n+m)}_{\boldsymbol{R}_1,\boldsymbol{R}_2,\ldots,\boldsymbol{R}_n,\boldsymbol{R}'_1,\boldsymbol{R}'_2,\ldots,\boldsymbol{R}'_m} P_{\boldsymbol{R}'_1}P_{\boldsymbol{R}'_2}\ldots P_{\boldsymbol{R}'_m}\\ &= V^{(n)}_{\boldsymbol{R}_1,\boldsymbol{R}_2,\ldots,\boldsymbol{R}_n} + \sum_{\boldsymbol{R}'_1} V^{(n+1)}_{\boldsymbol{R}_1,\boldsymbol{R}_2,\ldots,\boldsymbol{R}_n,\boldsymbol{R}'_1} P_{\boldsymbol{R}'_1}\\ &\quad + \frac{1}{2}\sum_{\boldsymbol{R}'_1,\boldsymbol{R}'_2} V^{(n+2)}_{\boldsymbol{R}_1,\boldsymbol{R}_2,\ldots,\boldsymbol{R}_n,\boldsymbol{R}'_1,\boldsymbol{R}'_2} P_{\boldsymbol{R}'_1}P_{\boldsymbol{R}'_2} + \cdots. \end{aligned} \tag{8.8}$$

It is easy to show that for any $n = 0, 1, \ldots$

$$\varphi^{(n)}_{\boldsymbol{R}_1,\boldsymbol{R}_2,\ldots,\boldsymbol{R}_n}(\{P_{\boldsymbol{R}}\}) = \frac{\partial\varphi^{(n-1)}_{\boldsymbol{R}_1,\boldsymbol{R}_2,\ldots,\boldsymbol{R}_{n-1}}(\{P_{\boldsymbol{R}}\})}{\partial P_{\boldsymbol{R}_n}} = \cdots = \frac{\partial^n}{\partial P_{\boldsymbol{R}_1}\partial P_{\boldsymbol{R}_2}\ldots\partial P_{\boldsymbol{R}_n}}\varphi^{(0)}(\{P_{\boldsymbol{R}}\}). \tag{8.9}$$

Taking into account that (see (4.5), (8.2) and (8.8))

$$\varphi^{(n)}_{\boldsymbol{R}_1,\boldsymbol{R}_2,\ldots,\boldsymbol{R}_n}(\{P_{\boldsymbol{R}}\})|_{P_{\boldsymbol{R}}=c} = \Phi^{(n)}_{\boldsymbol{R}_1,\boldsymbol{R}_2,\ldots,\boldsymbol{R}_n} \tag{8.10}$$

we have

$$\Phi^{(n)}_{\boldsymbol{R}_1,\boldsymbol{R}_2,\ldots,\boldsymbol{R}_n} = \frac{\partial^n}{\partial P_{\boldsymbol{R}_1}\partial P_{\boldsymbol{R}_2}\ldots\partial P_{\boldsymbol{R}_n}}\varphi^{(0)}(\{P_{\boldsymbol{R}}\})|_{P_{\boldsymbol{R}}=c}. \tag{8.11}$$

Substituting the functional $\Phi^{(0)}(\{P_{\boldsymbol{R}}\})$ calculated within the mean-field concentration functional theory into (8.11), one can obtain the potential $\Phi^{(n)}_{\boldsymbol{R}_1,\boldsymbol{R}_2,\ldots,\boldsymbol{R}_n}$ as well as its Fourier transform $\tilde{\Phi}^{(n)}_{\boldsymbol{k}_1,\boldsymbol{k}_2,\ldots,\boldsymbol{k}_{n-1}}$ (see (8.4)) for any order n. For application of the generalized ring approximation, it is sufficient to calculate the Fourier transforms $\tilde{\phi}^{(n)}_{\boldsymbol{k}_1,\boldsymbol{k}_2,\ldots,\boldsymbol{k}_{n-1}}$ for $n = 2, 3, 4$. Moreover, in the case of negligible contribution from the nonpair atomic interactions, it is sufficient to calculate only $\tilde{\Phi}^{(2)}_{\boldsymbol{k}}$ (see (7.11), (7.12)). Note that, for calculations within the generalized spherical model approximation (6.4), it is sufficient to calculate only $\tilde{\Phi}^{(2)}_{\boldsymbol{k}}$ in any case. The calculation of the potentials $\Phi^{(n)}_{\boldsymbol{R}_1,\boldsymbol{R}_2,\ldots,\boldsymbol{R}_n}$ for $n > 2$ is also helpful for estimation of the comparative contribution from the nonpair atomic interactions (see (8.2)).

In conclusion of this subsection, it should be emphasized that, despite the mean-field character of the concentration functional theory (which allows us to retain the electronic interactions in their full generality [32]), the use of it in combination with the generalized ring approximation permits us to go beyond the mean-field framework.

8.3. Connolly–Williams method

Within this method [29, 30], either the expression (2.1) or (more frequently) the following one

$$
\begin{aligned}
H &= J^{(0)} + \sum_{n=1}^{N} \frac{1}{n!} \sum_{\boldsymbol{R}_1,\boldsymbol{R}_2,\ldots,\boldsymbol{R}_n} J^{(n)}_{\boldsymbol{R}_1,\boldsymbol{R}_2,\ldots,\boldsymbol{R}_n} S_{\boldsymbol{R}_1} S_{\boldsymbol{R}_2} \ldots S_{\boldsymbol{R}_n} \\
&= J^{(0)} + \sum_{\boldsymbol{R}} J^{(1)}_{\boldsymbol{R}} S_{\boldsymbol{R}} + \frac{1}{2} \sum_{\boldsymbol{R}_1,\boldsymbol{R}_2} J^{(2)}_{\boldsymbol{R}_1,\boldsymbol{R}_2} S_{\boldsymbol{R}_1} S_{\boldsymbol{R}_2} \\
&\quad + \frac{1}{6} \sum_{\boldsymbol{R}_1,\boldsymbol{R}_2,\boldsymbol{R}_3} J^{(3)}_{\boldsymbol{R}_1,\boldsymbol{R}_2,\boldsymbol{R}_3} S_{\boldsymbol{R}_1} S_{\boldsymbol{R}_2} S_{\boldsymbol{R}_3} + \cdots
\end{aligned}
\tag{8.12}
$$

is used as for the Hamiltonian of the system under consideration. In (8.12) (see [1]):

$$
\begin{aligned}
J^{(n)}_{\boldsymbol{R}_1,\boldsymbol{R}_2,\ldots,\boldsymbol{R}_n} &= \sum_{m=0}^{N-n} \frac{1}{2^{n+m} m!} \sum_{\boldsymbol{R}'_1,\boldsymbol{R}'_2,\ldots,\boldsymbol{R}'_m} V^{(n+m)}_{\boldsymbol{R}_1,\boldsymbol{R}_2,\ldots,\boldsymbol{R}_n,\boldsymbol{R}'_1,\boldsymbol{R}'_2,\ldots,\boldsymbol{R}'_m} \\
&= \frac{1}{2^n} \left[V^{(n)}_{\boldsymbol{R}_1,\boldsymbol{R}_2,\ldots,\boldsymbol{R}_n} + \frac{1}{2} \sum_{\boldsymbol{R}'_1} V^{(n+1)}_{\boldsymbol{R}_1,\boldsymbol{R}_2,\ldots,\boldsymbol{R}_n,\boldsymbol{R}'_1} + \frac{1}{8} \sum_{\boldsymbol{R}'_1\boldsymbol{R}'_2} V^{(n+2)}_{\boldsymbol{R}_1,\boldsymbol{R}_2,\ldots,\boldsymbol{R}_n,\boldsymbol{R}'_1,\boldsymbol{R}'_2} + \cdots \right]
\end{aligned}
\tag{8.13}
$$

$$
S_{\boldsymbol{R}} = \begin{cases} 1 & \text{if on A-type atom is at site } \boldsymbol{R} \\ -1 & \text{otherwise.} \end{cases}
\tag{8.14}
$$

The potentials $V^{(n)}_{\boldsymbol{R}_1,\boldsymbol{R}_2,\ldots,\boldsymbol{R}_n}$ or $J^{(n)}_{\boldsymbol{R}_1,\boldsymbol{R}_2,\ldots,\boldsymbol{R}_n}$ are just those that are calculated within the Connolly–Williams method. The functions $\tilde{\Phi}^{(n)}_{\boldsymbol{k}_1,\boldsymbol{k}_2,\ldots,\boldsymbol{k}_{n-1}}$ (the knowledge of which for $n = 2$ and $n = 2, 3, 4$ is necessary for application of the generalized spherical model and ring approximations, respectively) can be expressed in terms of both the corresponding Fourier transforms $\tilde{V}^{(t)}_{\boldsymbol{k}_1,\boldsymbol{k}_2,\ldots,\boldsymbol{k}_{t-1}}$ (see (7.9), (7.13)–(7.15)) and $\tilde{J}^{(n)}_{\boldsymbol{k}_1,\boldsymbol{k}_2,\ldots,\boldsymbol{k}_{n-1}}$:

$$
\begin{aligned}
\tilde{\Phi}^{(n)}_{\boldsymbol{k}_1,\boldsymbol{k}_2,\ldots,\boldsymbol{k}_{n-1}} &= 2^n \sum_{l=0}^{N-n} \frac{(-1)^l (1-2c)^l}{l!} \tilde{J}^{(n+l)}_{\boldsymbol{k}_1,\boldsymbol{k}_2,\ldots,\boldsymbol{k}_{n-1},\boldsymbol{0},\boldsymbol{0},\ldots,\boldsymbol{0}} \\
&= 2^n \left[\tilde{J}^{(n)}_{\boldsymbol{k}_1,\boldsymbol{k}_2,\ldots,\boldsymbol{k}_{n-1}} - (1-2c) \tilde{J}^{(n-1)}_{\boldsymbol{k}_1,\boldsymbol{k}_2,\ldots,\boldsymbol{k}_{n-1},\boldsymbol{0}} + \frac{(1-2c)^2}{2} \tilde{J}^{(n+2)}_{\boldsymbol{k}_1,\boldsymbol{k}_2,\ldots,\boldsymbol{k}_{n-1},\boldsymbol{0},\boldsymbol{0}} - \cdots \right]
\end{aligned}
\tag{8.15}
$$

where

$$
\tilde{J}^{(n)}_{\boldsymbol{k}_1,\boldsymbol{k}_2,\ldots,\boldsymbol{k}_{n-1}} = \sum_{\boldsymbol{R}_1,\boldsymbol{R}_2,\ldots,\boldsymbol{R}_{n-1}} J^{(n)}_{\boldsymbol{R}_1,\boldsymbol{R}_2,\ldots,\boldsymbol{R}_{n-1},\boldsymbol{0}} \exp\left(-\mathrm{i} \sum_{l=1}^{n-1} \boldsymbol{k}_l \cdot \boldsymbol{R}_l \right).
\tag{8.16}
$$

With the aim of practical use within the generalized spherical model and ring approximations, let us write down the expressions for the functions $\tilde{\Phi}^{(n)}_{\boldsymbol{k}_1,\boldsymbol{k}_2,\ldots,\boldsymbol{k}_{n-1}}$ at $n = 2, 3, 4$ in terms of the Fourier transforms $\tilde{J}^{(n)}_{\boldsymbol{k}_1,\boldsymbol{k}_2,\ldots,\boldsymbol{k}_{n-1}}$ taking into account only pair, triplet and quadruplet atomic interactions:

$$
\tilde{\Phi}^{(2)}_{\boldsymbol{k}} = 4 \left[\tilde{J}^{(2)}_{\boldsymbol{k}} - (1-2c) \tilde{J}^{(3)}_{\boldsymbol{k},\boldsymbol{0}} + \frac{(1-2c)^2}{2} \tilde{J}^{(4)}_{\boldsymbol{k},\boldsymbol{0},\boldsymbol{0}} \right]
\tag{8.17}
$$

$$
\tilde{\Phi}^{(3)}_{\boldsymbol{k}_1,\boldsymbol{k}_2} = 8 [\tilde{J}^{(3)}_{\boldsymbol{k}_1,\boldsymbol{k}_2} - (1-2c) \tilde{J}^{(4)}_{\boldsymbol{k}_1,\boldsymbol{k}_2,\boldsymbol{0}}]
\tag{8.18}
$$

$$
\tilde{\Phi}^{(4)}_{\boldsymbol{k}_1,\boldsymbol{k}_2,\boldsymbol{k}_3} = 16 \tilde{J}^{(4)}_{\boldsymbol{k}_1,\boldsymbol{k}_2,\boldsymbol{k}_3}.
\tag{8.19}
$$

Note that the generalized spherical model and ring approximations can be directly applied in combination with the mixed-space cluster expansion within the Connolly–Williams method (see, e.g., [10, 30, 46]), because the data on the interatomic potentials both in real and reciprocal space forms may be used as the input data within these approximations.

9. Symmetry aspects

In section 4 of [35], the majority of the symmetry properties of the Fourier transforms of the mixing potentials was obtained. Let us derive one more such property.

Beginning with the definition (4.7a), we have (see equation (28) in [35])

$$\tilde{V}^{(n)}_{\boldsymbol{k}_1,\boldsymbol{k}_2,\ldots,\boldsymbol{k}_{n-1}} = \sum_{\boldsymbol{R}_1,\boldsymbol{R}_2,\ldots,\boldsymbol{R}_{n-1}} \tilde{V}^{(n)}_{\boldsymbol{R}_1,\boldsymbol{R}_2,\ldots,\boldsymbol{R}_n} \exp\left[-\mathrm{i}\sum_{l=1}^{n-1} \boldsymbol{k}_l\cdot(\boldsymbol{R}_l-\boldsymbol{R}_n)\right]. \tag{9.1}$$

Introducing the new variables of summation $\boldsymbol{R}'_l$ ($l = 2, 3, \ldots, n$)

$$\boldsymbol{R}'_l = \boldsymbol{R}_l - \boldsymbol{R}_1 \tag{9.2}$$

into (9.1), we obtain

$$\begin{aligned}\tilde{V}^{(n)}_{\boldsymbol{k}_1,\boldsymbol{k}_2,\ldots,\boldsymbol{k}_{n-1}} &= \sum_{\boldsymbol{R}'_2,\boldsymbol{R}'_3,\ldots,\boldsymbol{R}'_n} \tilde{V}^{(n)}_{\boldsymbol{0},\boldsymbol{R}'_2,\boldsymbol{R}'_3,\ldots,\boldsymbol{R}'_n} \exp\left[-\mathrm{i}\left(\sum_{l=2}^{n-1}\boldsymbol{k}_l\cdot\boldsymbol{R}'_l - \sum_{p=1}^{n-1}\boldsymbol{k}_p\cdot\boldsymbol{R}'_n\right)\right]\\ &= \tilde{V}^{(n)}_{-\sum_{p=1}^{n-1}\boldsymbol{k}_p,\boldsymbol{k}_2,\ldots,\boldsymbol{k}_{n-1}}.\end{aligned} \tag{9.3}$$

In the same way, introducing the following new variables of summation $\boldsymbol{R}'_l$ ($l = 2, 3, \ldots, t-1, t+1, \ldots, n$)

$$\boldsymbol{R}'_l = \boldsymbol{R}_l - \boldsymbol{R}_t \tag{9.4}$$

where t successively takes the values $2, 3, \ldots, n$ ($t = 1$ corresponds to (9.2)), into (9.1), one can prove the following relationships ($n = 2, 3, \ldots$; $i = 1, 2, \ldots, n-1$)

$$\tilde{V}^{(n)}_{\boldsymbol{k}_1,\boldsymbol{k}_2,\ldots,\boldsymbol{k}_{n-1}} = \tilde{V}^{(n)}_{\boldsymbol{k}_1,\boldsymbol{k}_2,\ldots,\boldsymbol{k}_{i-1},-\sum_{p=1}^{n-1}\boldsymbol{k}_p,\boldsymbol{k}_{i+1},\ldots,\boldsymbol{k}_{n-1}}. \tag{9.5}$$

Thus, the Fourier transform of the mixing potential is not changed under the replacement of any of its variables by the sum of all its variables with the opposite sign. So, from (9.5), for example, we have:

$$\tilde{V}^{(3)}_{\boldsymbol{k}_1,\boldsymbol{k}_2} = \tilde{V}^{(3)}_{\boldsymbol{k}_1,-(\boldsymbol{k}_1+\boldsymbol{k}_2)} = \tilde{V}^{(3)}_{-(\boldsymbol{k}_1+\boldsymbol{k}_2),\boldsymbol{k}_2}. \tag{9.6}$$

Note that in derivation of the expressions (6.4), (7.6) and (7.7) corresponding to the generalized spherical model and ring approximations, the relationships (9.5) were used. By use of (9.5) as well as of the other symmetry properties of the Fourier transforms of the mixing potentials [35], those expressions can be also transformed to other equivalent forms.

In section 5 of [1], it was noticed that the Hamiltonian (2.1) is invariant with respect to the exchange A ↔ B, because the designation of two sorts of atoms by symbols A and B is an arbitrary procedure. From comparison (2.1) and (8.5), it is evident that the functional $\varphi^{(0)}(\{P_{\boldsymbol{R}}\})$ has the same invariance. By use of this statement as well as (8.11), one may conclude that

$$\mathrm{A} \leftrightarrow \mathrm{B} \Rightarrow \Phi^{(n)}_{\boldsymbol{R}_1,\boldsymbol{R}_2,\ldots,\boldsymbol{R}_n} \to (-1)^n\,\Phi^{(n)}_{\boldsymbol{R}_1,\boldsymbol{R}_2,\ldots,\boldsymbol{R}_n} \tag{9.7}$$

for $n = 0, 1, \ldots$. From (9.7), it follows that the expressions (6.4) and (7.6) are invariant with respect to the exchange A ↔ B and, therefore, the corresponding generalized spherical model and ring approximations preserve the initial symmetry of the Hamiltonian.

10. Conclusions

In the present paper, within the first order of a modified thermodynamic perturbation theory, by use of the thermodynamic fluctuation method, in addition to the generalized spherical model and the high-temperature approximations obtained in [1], the new generalized ring analytical approximation for calculations of the grand thermodynamic potential as well as of the SRO parameters and their Fourier transforms in disordered binary alloys with Bravais crystal lattices was derived. An alloy was considered in the framework of the lattice gas model with many-body atomic interactions of arbitrary orders and effective radii of action, and the inverse effective number of atoms interacting with one fixed atom as well as the inverse temperature were successively used as a small parameter of expansion. The details are described of the application of the obtained approximations in combination with three widely used approaches for calculation of interatomic potentials in alloys, the generalized perturbation [25–28] and Connolly–Williams [29, 30] methods as well as the mean-field concentration functional theory [31–33].

It seems to be important to compare the numerical accuracies of the obtained approximation in the case of both the simplest model systems and an actual alloy for which the necessary information concerning atomic interactions is available. This problem is solved elsewhere [47].

Note that the approach advanced in the present work may be also used for the derivation of subsequent approximations within the thermodynamic perturbation theory. Besides, it seems to be advisable to extend this approach to the case of a multicomponent alloy with a complex crystal lattice and/or with LRO. The elaborated formalism concerning the lattice gas model itself may be also useful in fields other than alloy theory (see the last paragraph in section 6 of [1]).

Acknowledgments

The author thanks Dr V N Bugaev, Dr V I Tokar and Dr I Tsatskis for helpful discussions. He is also grateful to Professor V B Molodkin and Dr A N Timoshevskii 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 1998 *J. Phys.: Condens. Matter* **10** 1505
[2] Krivoglaz M A 1957 *Zh. Eksp. Teor. Fiz.* **32** 1368 (Engl. transl. *Sov. Phys.–JETP* **5** 1115)
[3] Krivoglaz M A and Smirnov A A 1964 *The Theory of Order–Disorder in Alloys* (London: Macdonald)
[4] Krivoglaz M A 1969 *The Theory of X-Ray and Thermal Neutron Scattering From Real Crystals* (New York: Plenum)
[5] Krivoglaz M A 1996 *Diffuse Scattering of X-Rays and Thermal Neutrons by Fluctuational Ingomogeneities of Imperfect Crystals* (Berlin: Springer)
[6] Solal F, Caudron R, Ducastelle F, Finel A and Loiseau A 1987 *Phys. Rev. Lett.* **58** 2245
[7] Chepulskii R V and Bugaev V N 1998 *J. Phys. Chem. Solids* **59** 1469
[8] Ozoliņš V, Wolverton C and Zunger A 1997 *Phys. Rev. Lett.* **79** 955
[9] Wolverton C, Ozoliņš V and Zunger A 1998 *Phys. Rev.* B **57** 4332
[10] Ozoliņš V, Wolverton C and Zunger A 1998 *Phys. Rev.* B **57** 6427
[11] Tsatskis I 1998 *J. Phys.: Condens. Matter* **10** L145
[12] Tsatskis I and Salje E K H 1998 *J. Phys.: Condens. Matter* **10** 3791
[13] Le Bolloc'h D, Caudron R and Finel A 1998 *Phys. Rev.* B **57** 2801

[14] Tsatskis I 1998 *Phys. Lett.* A **241** 110
[15] Tsatskis I 1998 *Phil. Mag. Lett.* **78** 403
[16] Wolverton C and Zunger A 1995 *Phys. Rev.* B **51** 6876
[17] Chepulskii R V and Bugaev V N 1998 *Solid State Commun.* **105** 615
[18] Chepulskii R V and Bugaev V N 1998 *J. Phys.: Condens. Matter* **10** 7309
[19] Chepulskii R V and Bugaev V N 1998 *J. Phys.: Condens. Matter* **10** 7327
[20] Chepulskii R V 1998 *J. Phys. Chem. Solids* **59** 1473
[21] Brout R 1959 *Phys. Rev.* **115** 824
[22] Brout R 1960 *Phys. Rev.* **118** 1009
[23] Brout R 1961 *Phys. Rev.* **122** 469
[24] Brout R 1965 *Phase Transitions* (New York: Benjamin)
[25] Ducastelle F and Gautier F 1976 *J. Phys. F: Met. Phys.* **6** 2039
[26] Gonis A, Zhang X-G, Freeman A J, Turchi P, Stocks G M and Nicholson D M 1987 *Phys. Rev.* B **36** 4630
[27] Turchi P E A, Stocks G M, Butler W H, Nicholson D M and Gonis A 1988 *Phys. Rev.* B **37** 5982
[28] Ducastelle F 1991 *Order and Phase Stability in Alloys* (New York: Elsevier)
[29] Connolly J W D and Williams A R 1983 *Phys. Rev.* B **27** 5169
[30] Zunger A 1994 *Statics and Dynamics of Alloy Phase Transformations (NATO ASI Series)* ed P E A Turchi and A Gonis (New York: Plenum) p 361
[31] Gyorffy B L and Stocks G M 1983 *Phys. Rev. Lett.* **50** 374
[32] Stocks G M, Nicholson D M, Shelton W A, Gyorffy B L, Pinski F J, Johnson D D, Staunton J B, Ginatempu B, Turchi P E A and Sluiter M 1994 *Statics and Dynamics of Alloy Phase Transformations (NATO ASI Series)* ed P E A Turchi and A Gonis (New York: Plenum) p 305
[33] Staunton J B, Johnson D D and Pinski F J 1994 *Phys. Rev.* B **50** 1450
Johnson D D, Staunton J B and Pinski F J 1994 *Phys. Rev.* B **50** 1473
[34] Sanchez J M, Ducastelle F and Gratias D 1984 *Physica* A **128** 334
[35] Bugaev V N and Chepulskii R V 1995 *Acta Crystallogr.* A **51** 456
[36] Bugaev V N and Chepulskii R V 1995 *Acta Crystallogr.* A **51** 463
[37] Kirkwood J G 1938 *J. Chem. Phys.* **6** 70
[38] Badalyan D A and Khachaturyan A G 1970 *Fiz. Tverd. Tela* **12** 439
[39] Khachaturyan A G 1978 *J. Prog. Mater. Sci.* **22** 1
[40] de Fontaine D 1979 *Solid State Physics* vol 34 (New York: Academic) p 73
[41] Landau L D and Lifshitz E M 1980 *Course of Theoretical Physics* vol 5 (Oxford: Pergamon)
[42] Horwitz G and Callen H B 1961 *Phys. Rev.* **124** 1757
[43] Cowley J M 1950 *Phys. Rev.* **77** 669
[44] Warren B E 1969 *X-Ray Diffraction* (Reading, MA: Addison-Wesley)
[45] Badalyan D A, Muradyan A A and Melik-Vartanayn D K 1988 *Izv. Vuz. Fiz.* **31** (8) 62
[46] Lu Z W, Laks D B, Wei S-H and Zunger A 1994 *Phys. Rev.* B **50** 6642
[47] Chepulskii R V 1999 *J. Phys.: Condens. Matter* **11** 8661–71