

Statistical-thermodynamic description within the ring approximation. I. Lattice-gas model

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The general method is elaborated for the statistical-thermodynamic description within the ring approximation of the lattice gas with a complex crystal lattice and with nonpair atomic interactions of any order and effective radii of action. The ring approximation corresponds to 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. By the elaborated method one can calculate the complete phase diagram of the lattice gas as well as the correlation effects in both disordered and long-range ordered states of it. The elaborated method is general and analytically simple. The corresponding analytical expressions do not change their form at an increase of the effective radius of atomic interactions and are valid in case of any superstructure. The number of the “variational” parameters for minimization of the free energy is considerably fewer than that within the cluster-variation method and are determined by the type of the superstructure rather than by the value of the effective radius of atomic interactions. Due to the analytical nature of the ring approximation, the time for calculations within it is much less than that of the Monte Carlo simulation. By a comparison with the results of the Monte Carlo simulation the high numerical accuracy of the ring approximation is demonstrated in wide temperature-concentration intervals. The tendency of increase of the numerical accuracy of the ring approximation with increase of the effective radius of atomic interactions is shown. The applicability of the ring approximation is discussed. The obtained results may be useful for a description of solid solutions, alloys, magnetics, fluids, and amorphous materials.

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I. INTRODUCTION

The lattice-gas model¹ has proved to be useful for a description of solid solutions, alloys, magnetics, fluids, and amorphous materials. However, in many cases the atomic interactions in such systems are long ranged (for the case of alloys see, e.g., an introduction in Ref. 2). The Monte Carlo³ (MC) and cluster-variation⁴⁻⁷ high-accuracy methods, which are most widely used for the statistical-thermodynamic description of the lattice-gas model, encounter the computational difficulties in such cases (e.g., Ref. 8). The treatment of the long-ranged atomic interactions is not problematic within the mean-field and high-temperature approximations but the corresponding results have low numerical accuracy and can be inadequate even qualitatively (e.g., Refs. 4,9).

Brout¹⁰⁻¹³ suggested to use the quantity z^{-1} as a small parameter of expansion in the thermodynamic perturbation theory, where z is the effective number of atoms interacting with one fixed atom. Such a parameter of expansion can be expected to be useful for systems with long-range atomic interactions when z must be large. Besides, within such an approach the interaction parameters appear in the final expressions only through the Fourier transform of the interatomic potential. So there are no computational difficulties for consideration of long-range atomic interactions. Brout approach was elaborated in the case of a ferromagnetic state of the Ising model (with only pair spin interactions), which is equivalent to the disordered [i.e., without a long-range order (LRO)] lattice-gas model (e.g., Sec. 2.6 in Ref. 14).

In Refs. 2,15-18 the z^{-1} approximation (up to the first order) was used for study of the correlation effects in the

disordered lattice gas with a Bravais crystal lattice. The approximation was named as ring in accordance with the topology of the diagrams being taken into account within the approximation in the context of the corresponding diagram technique. In the cases of long-range atomic interactions, the high numerical accuracy of the ring approximation was obtained in wide temperature-concentration intervals (by a comparison with the MC simulation). In Ref. 19 the method was proposed for description of a LRO lattice gas with pair atomic interactions within the ring approximation.

The aim of the present paper is to elaborate the general method for the statistical-thermodynamic description within the ring approximation of a lattice gas with arbitrary complex crystal lattice and with many-body atomic interactions of any order and effective radii of action. (The importance of introduction of nonpair atomic interactions into the consideration was discussed, e.g., in Sec. 1 of Ref. 20.) In Sec. II, the configurational Hamiltonian is introduced for a description of the lattice gas. In Secs. III and IV, the expression for the free energy is obtained within the ring approximation. In Sec. V, the approximations within the lattice-gas model that are similar to the ring one are outlined. In Sec. VI, the applicability of the ring approximation is discussed. In Sec. VII, the equations of state for a determination of the thermodynamically stable or metastable superstructures are derived within the ring approximation. In Sec. VIII, the sufficient condition of the thermodynamical stability or metastability of the superstructures is studied. In Sec. IX, the expressions for the interatomic correlation functions are obtained within the ring approximation. In Sec. X, the method of calculation of the complete phase diagram of the lattice gas is proposed.

In Sec. XI, the applicability of the obtained results in the case of a multicomponent lattice gas is discussed. In Sec. XII, the expression for the heat capacity is obtained in the case of the disordered state. The numerical accuracy of the method is verified through the comparison with the corresponding data of MC simulation in Sec. XIII. In Sec. XIV, advantages and disadvantages of the ring approximation are summarized.

II. CONFIGURATIONAL HAMILTONIAN

Let us consider a two-component A - B lattice gas.¹ We suppose that the unit cell of the crystal lattice consists of ν sites ($\nu \geq 1$). It is important that the case of $\nu > 1$ can be attributed not only to the complex character of the crystal lattice itself but also to the presence of a LRO in atomic distribution. The crystal lattice can be divided into ν Bravais sublattices according with the unit cell. Taking into account the many-body atomic interactions of arbitrary orders and radii of action, the Hamiltonian H of the lattice gas in question can be written in the following form [e.g., Eq. (9) in Ref. 21]:

$$H = Nv_0 + \sum_{n=1}^{N\nu} \frac{1}{n!} \sum_{i_1, i_2, \dots, i_n} \sum_{\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_n} \times V_{i_1, \mathbf{R}_1; i_2, \mathbf{R}_2; \dots; i_n, \mathbf{R}_n}^{(n)} C_{i_1, \mathbf{R}_1} C_{i_2, \mathbf{R}_2} \cdots C_{i_n, \mathbf{R}_n}, \quad (1)$$

or writing the series explicitly,

$$\begin{aligned} H = Nv_0 + \sum_i V_i^{(1)} \sum_{\mathbf{R}} C_{i, \mathbf{R}} \\ + \frac{1}{2} \sum_{i_1, i_2} \sum_{\mathbf{R}_1, \mathbf{R}_2} V_{i_1, \mathbf{R}_1; i_2, \mathbf{R}_2}^{(2)} C_{i_1, \mathbf{R}_1} C_{i_2, \mathbf{R}_2} \\ + \frac{1}{6} \sum_{i_1, i_2, i_3} \sum_{\mathbf{R}_1, \mathbf{R}_2, \mathbf{R}_3} V_{i_1, \mathbf{R}_1; i_2, \mathbf{R}_2; i_3, \mathbf{R}_3}^{(3)} C_{i_1, \mathbf{R}_1} C_{i_2, \mathbf{R}_2} C_{i_3, \mathbf{R}_3} \\ + \dots \end{aligned} \quad (2)$$

In Eqs. (1) and (2), the summations on the indices i and on the site radius vectors \mathbf{R} are carried over all ν sublattices and over all N unit cells of the crystal lattice, respectively, $C_{i, \mathbf{R}}$ is the configurational variable

$$C_{i, \mathbf{R}} = \begin{cases} 1 & \text{if the site } (i, \mathbf{R}) \text{ is occupied by an} \\ & A\text{-type atom} \\ 0 & \text{otherwise} \end{cases} \quad (3)$$

(type B is excluded from the configurational description—see Sec. 2 in Ref. 21), v_0 is the energy per unit cell of the lattice gas in which all sites are occupied by B -type of atoms, $V_{i_1, \mathbf{R}_1; i_2, \mathbf{R}_2; \dots; i_n, \mathbf{R}_n}^{(n)}$ is the mixing potential of n th order ($n = 1, 2, \dots, N\nu$) [see Eq. (10) in Ref. 21].

In the configurational description of the lattice gas presented above we follow Refs. 9, 21–24 and cluster-variation method methodology, where each LRO structure (superstructure) is described in terms of its own unit cell (both in direct and reciprocal spaces) determined by the space symmetry of

that structure. Such a description allows to take easily into account the symmetry difference of the mixing potentials for different structures²¹ as well as to perform the summation of the infinite series in the cumulant expansion in a general form (see below Sec. IV). Our description is principally different from that one accepted in the method of static concentration waves (e.g., Refs. 25–29), where any superstructure is described in terms of the unit cell of the corresponding parent *disordered* structure.

III. FREE ENERGY

We describe our system within the grand canonical ensemble. The necessity of use of such an ensemble is discussed below in Sec. VI. The grand partition function Ξ of the lattice gas

$$\Xi \equiv \sum_{\{C_{i, \mathbf{R}}\}} \exp \left\{ -(k_B T)^{-1} \left[H - \sum_{i=1}^{\nu} (\mu_A^{(i)} N_A^{(i)} + \mu_B^{(i)} N_B^{(i)}) \right] \right\} \quad (4)$$

can be presented in the following form:

$$\Xi = \Xi_0 \sum_{\{C_{i, \mathbf{R}}\}} \exp \left[-\frac{X}{k_B T} \right], \quad (5)$$

where

$$\Xi_0 = \exp \left\{ -(k_B T)^{-1} N \left[v_0 - \sum_{i=1}^{\nu} \mu_B^{(i)} \right] \right\}, \quad (6)$$

$$\begin{aligned} X = \sum_{n=2}^{N\nu} \frac{1}{n!} \sum_{i_1, i_2, \dots, i_n} \sum_{\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_n} W_{i_1, \mathbf{R}_1; i_2, \mathbf{R}_2; \dots; i_n, \mathbf{R}_n}^{(n)} \\ \times C_{i_1, \mathbf{R}_1} C_{i_2, \mathbf{R}_2} \cdots C_{i_n, \mathbf{R}_n}, \end{aligned} \quad (7)$$

$$\begin{aligned} W_{i_1, \mathbf{R}_1; i_2, \mathbf{R}_2; \dots; i_n, \mathbf{R}_n}^{(n)} \\ = \begin{cases} V_{i_1, \mathbf{R}_1; i_2, \mathbf{R}_2}^{(2)} + \mu_{i_1} \delta_{i_1, i_2} \delta_{\mathbf{R}_1, \mathbf{R}_2} & \text{if } n=2 \\ V_{i_1, \mathbf{R}_1; i_2, \mathbf{R}_2; \dots; i_n, \mathbf{R}_n}^{(n)} & \text{if } n>2, \end{cases} \end{aligned} \quad (8)$$

$$\mu_i = 2[V_i^{(1)} - \mu_A^{(i)} + \mu_B^{(i)}], \quad (9)$$

$\mu_\alpha^{(i)}$ and $N_\alpha^{(i)}$ ($i = 1, 2, \dots, \nu$; $\alpha = A, B$) are the chemical potentials and the total numbers of α -type atoms at i th sublattice, respectively; T is the absolute temperature, k_B is the Boltzmann constant, the summation on $\{C_{i, \mathbf{R}}\}$ is carried over all possible atomic configurations, and δ is the Kronecker delta. At derivation of Eq. (5) the following relationships:

$$N_A^{(i)} + N_B^{(i)} = N, \quad N_A^{(i)} = \sum_{\mathbf{R}} C_{i, \mathbf{R}}, \quad (10)$$

$$[C_{i, \mathbf{R}}]^n = C_{i, \mathbf{R}}, \quad (11)$$

where n is a positive integer, were used. The symmetry equivalence of the crystal lattice sites *within* each sublattice was taken into account (see Sec. 3 in Ref. 21). We put dif-

ferent values for the chemical potentials of atoms at different sublattices assuming symmetry inequivalence of sublattices in general case. Such inequivalence is caused, for example, by space inhomogeneity in atom distribution due to the presence of a LRO.

Note that the expression (5) for the grand partition function can be converted into the expression for the *canonical* partition function formally by setting $\mu_i=0$ for all i (under neglect of the configuration-independent multiplier). This allows us, if need be, to make a step from the grand canonical description to the canonical one in the final expressions for statistical-thermodynamic characteristics of the lattice gas by setting $\mu_i=0$.

According to the Kirkwood methodology,³⁰ the expression for the grand thermodynamic potential Ω corresponding to the grand partition function (5) can be written as follows:

$$\Omega = -k_B T \ln \Xi = N \left[v_0 - \sum_{i=1}^{\nu} \mu_B^{(i)} \right] - k_B T \ln \Delta \Gamma + \Delta \Omega, \quad (12)$$

where

$$\Delta \Omega = -k_B T \ln \left\langle \exp \left[-\frac{X}{k_B T} \right] \right\rangle, \quad (13)$$

the sign $\langle \dots \rangle$ means the statistical average over all $\Delta \Gamma$ possible configurations

$$\langle \dots \rangle = \Delta \Gamma^{-1} \sum_{\{C_{i,\mathbf{R}}\}} \dots, \quad \Delta \Gamma = \sum_{\{C_{i,\mathbf{R}}\}}, \quad (14)$$

At a statistical-thermodynamic description of the lattice-gas model it is convenient to use the average sublattice atom concentrations P_i ($i=1,2,\dots,\nu$) rather than the chemical potentials as given (input) parameters:¹⁴

$$P_i = \langle C_{i,\mathbf{R}} \rangle_{\text{LRO}} = \langle N_A^{(i)} \rangle_{\text{LRO}} / N, \quad (15)$$

where sign $\langle \dots \rangle_{\text{LRO}}$ means the statistical average over all possible atomic configurations with a given LRO. Note that P_i is equal to the probability of finding an A -type atom at a site belonging to the i th sublattice and all the quantities P_i are independent of the radius vector \mathbf{R} of unit cell due to the translational invariance of unit cells. According to such a description, we move to the expression for the free energy f per unit cell of the system in question,

$$f = N^{-1} \left\{ \Omega + \sum_{i=1}^{\nu} [\mu_A^{(i)} \langle N_A^{(i)} \rangle_{\text{LRO}} + \mu_B^{(i)} \langle N_B^{(i)} \rangle_{\text{LRO}}] \right\}, \quad (16)$$

which can be presented in the form [by the use of Eq. (12)]

$$f = v_0 + \sum_i P_i \left[V_i^{(1)} - \frac{\mu_i}{2} \right] - N^{-1} k_B T \ln \Delta \Gamma + \Delta f, \quad (17)$$

where [see Eq. (13)]

$$\Delta f = \Delta \Omega / N. \quad (18)$$

The values of the chemical potentials $\{\mu_\alpha^{(i)}\}$ and, therefore [see Eq. (9)], the values of μ_i corresponding to given values of $\{P_i\}$ are found from the following standard relationships ($i=1,2,\dots,\nu$):

$$\langle N_\alpha^{(i)} \rangle_{\text{LRO}} = -\partial \Omega / \partial \mu_\alpha^{(i)}, \quad (19)$$

which transform into the following equations for determination of μ_i :

$$\partial f / \partial \mu_i = 0. \quad (20)$$

In such a description the quantities μ_i are intermediate just like μ in Fermi-Dirac distribution (e.g., Chap. 5 in Ref. 31).

IV. CUMULANT EXPANSION

According to the general approach of the thermodynamic perturbation theory (see Refs. 10–12,26,30,32–34 and Sec. 3 in Ref. 17), the expression (18) for Δf can be expanded in a cumulant series in powers of the inverse temperature,

$$\Delta f = -\frac{k_B T}{N} \ln \left\langle \exp \left[-\frac{X}{k_B T} \right] \right\rangle = -\frac{k_B T}{N} \sum_{n=1}^{\infty} \frac{1}{n!} \frac{M_n(X)}{(-k_B T)^n}, \quad (21)$$

where $M_n(X)$ is the cumulant of n th order.

The expression (7) for X converts to the corresponding expression (3.2) in Ref. 17 by the transformation

$$(i, \mathbf{R}) \rightarrow \mathbf{R}. \quad (22)$$

It is easy to show that the final results obtained in Sec. 3 of Ref. 17 are also valid for more general case being considered in the present paper if one performs the transformation (22) in those results. Taking this fact into account and following to the Brout approach^{10–12} (see also Secs. 5–7 in Ref. 17), let us select the contributions Δf_0 and Δf_1 to the cumulant expansion (21) from the irreducible summands proportional, respectively, to the zeroth and first powers of the quantity z^{-1} , with z being equal to the effective number of atoms interacting with one fixed atom,

$$\Delta f_0 = \frac{1}{N} \sum_{n=2}^{N\nu} \frac{1}{n!} \sum_{i_1, i_2, \dots, i_n} \sum_{\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_n} \times W_{i_1, \mathbf{R}_1; i_2, \mathbf{R}_2; \dots; i_n, \mathbf{R}_n}^{(n)} \tilde{P}_{i_1} \tilde{P}_{i_2} \dots \tilde{P}_{i_n}, \quad (23)$$

$$\Delta f_1 = -\frac{k_B T}{2N} \sum_{n=1}^{\infty} \frac{1}{n} \sum_{i_1, i_2, \dots, i_n} \sum_{\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_n} \times f_{\mathbf{R}_1 - \mathbf{R}_2}^{i_1, i_2} f_{\mathbf{R}_2 - \mathbf{R}_3}^{i_2, i_3} \dots f_{\mathbf{R}_n - \mathbf{R}_1}^{i_n, i_1}, \quad (24)$$

where

$$\tilde{P}_i = \langle C_{i,\mathbf{R}} \rangle, \quad (25)$$

$$f_{\mathbf{R}_l - \mathbf{R}_m}^{i_l, i_m} = - \frac{\sqrt{\tilde{P}_{i_l}(1-\tilde{P}_{i_l})}(\mu_{i_l}\delta_{i_l, i_m}\delta_{\mathbf{R}_l, \mathbf{R}_m} + \Phi_{\mathbf{R}_l - \mathbf{R}_m}^{i_l, i_m})\sqrt{\tilde{P}_{i_m}(1-\tilde{P}_{i_m})}}{k_B T}, \quad (26)$$

$$\Phi_{\mathbf{R}_l - \mathbf{R}_m}^{i_l, i_m} = \sum_{t=0}^{N\nu-2} \sum_{i'_1, i'_2, \dots, i'_t} \frac{\tilde{P}_{i'_1}\tilde{P}_{i'_2}\dots\tilde{P}_{i'_t}}{t!} \sum_{\mathbf{R}'_1, \mathbf{R}'_2, \dots, \mathbf{R}'_t} V_{i'_1, \mathbf{R}'_1; i'_2, \mathbf{R}'_2; \dots; i'_t, \mathbf{R}'_t; i_l, \mathbf{R}_l; i_m, \mathbf{R}_m}^{(2+t)}. \quad (27)$$

Note that Eqs. (23) and (24) are similar to Eqs. (6.2) and (7.2) in Ref. 17, respectively. Nevertheless, there is a principal difference between them. Namely, Eqs. (23) and (24) of the present paper correspond to the initially LRO state whereas Eqs. (6.2) and (7.2) in Ref. 17 correspond to the initially disordered state with fluctuating LRO (see also Sec. VII below).

Let us approximately put (see below a discussion in Sec. VI)

$$\tilde{P}_i \approx P_i, \quad \ln \Delta \Gamma \approx \ln \Delta \Gamma_{\text{LRO}}, \quad (28)$$

where $\Delta \Gamma_{\text{LRO}}$ is the number of configurations corresponding to a state with a given LRO (e.g., Refs. 4,26,30),

$$\ln \Delta \Gamma_{\text{LRO}} = -N \sum_{i=1}^{\nu} [P_i \ln P_i + (1-P_i) \ln(1-P_i)]. \quad (29)$$

Introducing the Fourier transforms

$$\tilde{V}_{i_1, \mathbf{k}_1; i_2, \mathbf{k}_2; \dots; i_{n-1}, \mathbf{k}_{n-1}; i_n}^{(n)}$$

of the mixing potentials ($n=2,3, \dots, N\nu$)

$$\begin{aligned} \tilde{V}_{i_1, \mathbf{k}_1; i_2, \mathbf{k}_2; \dots; i_{n-1}, \mathbf{k}_{n-1}; i_n}^{(n)} &= \sum_{\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_{n-1}} V_{i_1, \mathbf{R}_1; i_2, \mathbf{R}_2; \dots; i_{n-1}, \mathbf{R}_{n-1}; i_n, \mathbf{0}}^{(n)} \\ &\times \exp \left[-i \sum_{i=1}^{n-1} \mathbf{k}_i \mathbf{R}_i \right], \end{aligned}$$

$$\begin{aligned} V_{i_1, \mathbf{R}_1; i_2, \mathbf{R}_2; \dots; i_{n-1}, \mathbf{R}_{n-1}; i_n, \mathbf{R}_n}^{(n)} &= \frac{1}{N^{n-1}} \sum_{\mathbf{k}_1, \mathbf{k}_2, \dots, \mathbf{k}_{n-1}} \tilde{V}_{i_1, \mathbf{k}_1; i_2, \mathbf{k}_2; \dots; i_{n-1}, \mathbf{k}_{n-1}; i_n}^{(n)} \\ &\times \exp \left[i \sum_{i=1}^{n-1} \mathbf{k}_i (\mathbf{R}_i - \mathbf{R}_n) \right], \end{aligned} \quad (30)$$

and performing a number of matrix transformations (see Appendix A), one can obtain

$$\begin{aligned} \Delta f_0 &= \frac{1}{2} \sum_i \mu_i P_i^2 + \sum_{n=2}^{N\nu} \frac{1}{n!} \sum_{i_1, i_2, \dots, i_n} \tilde{V}_{i_1, \mathbf{0}; i_2, \mathbf{0}; \dots; i_{n-1}, \mathbf{0}; i_n}^{(n)} \\ &\times P_{i_1} P_{i_2} \dots P_{i_n}, \end{aligned} \quad (31)$$

$$\Delta f_1 = \frac{k_B T}{2N} \sum_{\mathbf{k}} \ln \det A_{\mathbf{k}}, \quad (32)$$

where the summations on \mathbf{k} are carried over all the points specified by the cyclic boundary conditions in the corresponding first Brillouin zone and the designation $\det A_{\mathbf{k}}$ means the determinant of the matrix $A_{\mathbf{k}}$ with the following elements:

$$\begin{aligned} A_{\mathbf{k}}^{i_1, i_2} &= \delta_{i_1, i_2} \\ &+ \frac{\sqrt{P_{i_1}(1-P_{i_1})}[\mu_{i_1}\delta_{i_1, i_2} + \Phi_{i_1, \mathbf{k}; i_2}^{(2)}]\sqrt{P_{i_2}(1-P_{i_2})}}{k_B T}. \end{aligned} \quad (33)$$

The function $\Phi_{i_1, \mathbf{k}; i_2}^{(2)}$ in Eq. (33) corresponds to the particular case $n=2$ [see Eq. (B3) in Appendix B] of the more general function $\Phi_{i_1, \mathbf{k}_1; i_2, \mathbf{k}_2; \dots; i_{n-1}, \mathbf{k}_{n-1}; i_n}^{(n)}$ ($n=0,1, \dots, N\nu$)

$$\begin{aligned} \Phi_{i_1, \mathbf{k}_1; i_2, \mathbf{k}_2; \dots; i_{n-1}, \mathbf{k}_{n-1}; i_n}^{(n)} &= \sum_{t=0}^{N\nu-n} \frac{1}{t!} \sum_{i'_1, i'_2, \dots, i'_t} P_{i'_1} P_{i'_2} \dots P_{i'_t} \\ &\times \tilde{V}_{i'_1, \mathbf{0}; i'_2, \mathbf{0}; \dots; i'_t, \mathbf{0}; i_1, \mathbf{k}_1; i_2, \mathbf{k}_2; \dots; i_{n-1}, \mathbf{k}_{n-1}; i_n}^{(t+n)}, \end{aligned} \quad (34)$$

which will be necessary below.

A. Mean-field (MF) approximation

Let us take into account only the contribution Δf_0 to the cumulant expansion. According to the Brout approach¹⁰⁻¹² (see also Secs. 5-7 in Ref. 17) such a contribution is proportional to the zeroth power of the quantity z^{-1} , with z being equal to the effective number of atoms interacting with one fixed atom. Below in Sec. VI, it is shown that within the approximations that take into account the finite numbers of terms in the cumulant expansion, it is correct to use the *canonical* ensemble. As it was noticed in Sec. III, we can move to the canonical formalism putting $\mu_i=0$ for any i in the final expressions obtained within the grand canonical formalism. On such a way substituting Eq. (31) instead of Δf into Eq. (17), we get the well known MF approximation

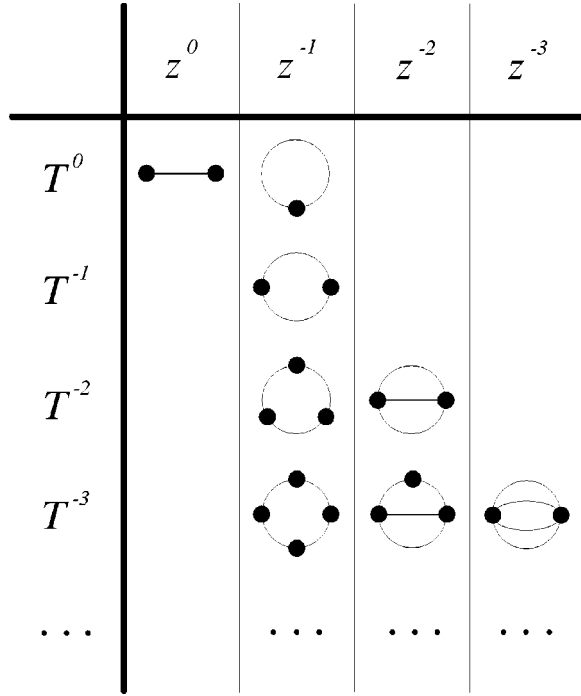


FIG. 1. Classification by powers of T^{-1} and z^{-1} of the linked irreducible diagrams corresponding to the terms in the cumulant expansion (see Sec. 3 in Ref. 2).

$$f_{\text{MF}} = \varepsilon_{\text{MF}} - T s_{\text{MF}}, \quad (35)$$

where [see Eqs. (34) and (B1) in Appendix B]

$$\varepsilon_{\text{MF}} = \Phi^{(0)}, \quad (36)$$

$$s_{\text{MF}} = -k_{\text{B}} \sum_{i=1}^{\nu} [P_i \ln P_i + (1 - P_i) \ln(1 - P_i)]. \quad (37)$$

B. Ring approximation

Let us take into account both contributions Δf_0 and Δf_1 to the cumulant expansion. According to the Brout approach¹⁰⁻¹² (see also Secs. 5-7 in Ref. 17) those irreducible contributions are proportional to the zeroth and first powers of the quantity z^{-1} , with z being equal to the effective number of atoms interacting with one fixed atom. We shall call such an approximation as the ring approximation. Note that such name is in accordance with the topology of the diagrams corresponding to Δf_1 in the context of the developed diagram technique [see Eq. (7.1) in Ref. 17 and Fig. 1 of the present paper].

In that case substituting Eqs. (31) and (32) instead of Δf into Eq. (17), we obtain the following expression for the free energy within the ring approximation:³⁵

$$f_{\text{ring}} = f_{\text{MF}} - \frac{1}{2} \sum_i \mu_i P_i (1 - P_i) + \frac{k_{\text{B}} T}{2N} \sum_{\mathbf{k}} \ln \det A_{\mathbf{k}}, \quad (38)$$

where f_{MF} is defined in Eq. (35) and the quantities μ_i are to be determined from the equations ($i = 1, 2, \dots, \nu$)

$$N^{-1} \sum_{\mathbf{k}} \|A_{\mathbf{k}}^{-1}\|_{ii} = 1. \quad (39)$$

Equation (39) was derived from Eq. (20) at substitution of f_{ring} instead of f . The designation $\|A_{\mathbf{k}}^{-1}\|_{ii}$ means the i th diagonal element of the matrix $A_{\mathbf{k}}^{-1}$ inverse to $A_{\mathbf{k}}$, which is defined in Eq. (33). By a symmetry consideration, it is easy to show that one may use the matrix $\tilde{A}_{\mathbf{k}}$ with the following elements:

$$\tilde{A}_{\mathbf{k}}^{i_1, i_2} = \delta_{i_1, i_2} + \frac{P_{i_1} (1 - P_{i_1})}{k_{\text{B}} T} [\mu_{i_1} \delta_{i_1, i_2} + \Phi_{i_1, \mathbf{k}; i_2}^{(2)}], \quad (40)$$

instead of $A_{\mathbf{k}}$ in Eqs. (38) and (39).

From Eq. (38) one can obtain the following expressions for the energy $\varepsilon_{\text{ring}}$ and entropy s_{ring} within the ring approximation:

$$\varepsilon_{\text{ring}} = \varepsilon_{\text{MF}} - \frac{1}{2} \sum_i \mu_i P_i (1 - P_i), \quad (41)$$

$$s_{\text{ring}} = s_{\text{MF}} - \frac{k_{\text{B}}}{2N} \sum_{\mathbf{k}} \ln \det A_{\mathbf{k}}, \quad (42)$$

where ε_{MF} and s_{MF} are determined in Eqs. (36) and (37), respectively.

C. Case of the disordered lattice gas with a Bravais crystal lattice

In such a case, $P_i = c$ (c is the total concentration of A-type atoms), and it is not necessary to introduce the sublattice index i . Instead of (35) and (38) we have within the MF approximation and ring approximations, respectively,

$$f_{\text{MF}} = v_0 + c V^{(1)} + \sum_{n=2}^{N\nu} \frac{c^n}{n!} \tilde{V}_{\mathbf{0}, \mathbf{0}, \dots, \mathbf{0}}^{(n)} + k_{\text{B}} T [c \ln c + (1 - c) \ln(1 - c)], \quad (43)$$

$$f_{\text{ring}} = f_{\text{MF}} - \frac{1}{2} \mu c (1 - c) + \frac{k_{\text{B}} T}{2N} \sum_{\mathbf{k}} \ln \left\{ 1 + \frac{c(1 - c)}{k_{\text{B}} T} [\mu + \Phi_{\mathbf{k}}^{(2)}] \right\}, \quad (44)$$

where the quantity μ is to be determined from the equation

$$N^{-1} \sum_{\mathbf{k}} \left\{ 1 + \frac{c(1 - c)}{k_{\text{B}} T} [\mu + \Phi_{\mathbf{k}}^{(2)}] \right\}^{-1} = 1, \quad (45)$$

$$\begin{aligned} \tilde{\Phi}_{\mathbf{k}_1, \mathbf{k}_2, \dots, \mathbf{k}_{n-1}}^{(n)} &= \sum_{t=0}^{N\nu-n} \frac{c^t}{t!} \tilde{V}_{\mathbf{0}, \mathbf{0}, \dots, \mathbf{0}, \mathbf{k}_1, \mathbf{k}_2, \dots, \mathbf{k}_{n-1}}^{(t+n)} \\ &= \tilde{V}_{\mathbf{k}_1, \mathbf{k}_2, \dots, \mathbf{k}_{n-1}}^{(n)} + c \tilde{V}_{\mathbf{0}, \mathbf{k}_1, \mathbf{k}_2, \dots, \mathbf{k}_{n-1}}^{(1+n)} \\ &\quad + c^2 / 2 \tilde{V}_{\mathbf{0}, \mathbf{0}, \mathbf{k}_1, \mathbf{k}_2, \dots, \mathbf{k}_{n-1}}^{(2+n)} + \dots, \end{aligned} \quad (46)$$

$$\begin{aligned} \tilde{V}_{\mathbf{k}_1, \mathbf{k}_2, \dots, \mathbf{k}_{n-1}}^{(n)} &= \sum_{\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_{n-1}} V_{\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_{n-1}, 0}^{(n)} \\ &\times \exp \left[-i \sum_{i=1}^{n-1} \mathbf{k}_i \mathbf{R}_i \right]. \end{aligned} \quad (47)$$

Note that Eqs. (46) and (47) are the particular cases of Eqs. (34) and (30). The expressions for the energy and entropy are obvious in the considered case.

V. SIMILAR APPROXIMATIONS

Let us outline the approximations within the lattice-gas model that are similar to the ring one. (In the case of the Ising model the same will be done in Ref. 36.)

In the particular case of only pair atomic interactions, expression (38) transforms into Eqs. (3) and (12) in Ref. 19.

In Ref. 24, by integration of the equations of state of the Onsager cavity field approximation,^{37,38} the expressions for the free energy were obtained in the case of the disordered state, $L1_0$ and $L1_2$ structures of the face-centered-cubic (fcc) lattice gas. Those expressions are similar to the corresponding expressions obtained within the ring approximation when nonpair atomic interactions are neglected. Unfortunately, a general expression for the free energy of arbitrary superstructure was not obtained in Ref. 24.

In Ref. 23 (Secs. 3.2.2 and 3.4 there), within both Brout approach and collective variables method, the expression for the free energy of arbitrary superstructure was obtained. Besides, in Ref. 39 (see also Ref. 40), by the collective variables method within the Gaussian approximation, the expression for the free energy of the *disordered* lattice gas with a complex crystal lattice was obtained. The corresponding expressions in Refs. 23,39 and those obtained within the ring approximation are not identical but have common features. The expressions obtained within the ring approximation seem to be mathematically simpler. In the case of the disordered lattice gas with a Bravais crystal lattice and with only pair atomic interactions, both expressions in Refs. 23,39 transform into the corresponding equation (44) obtained within the ring approximation.

In Refs. 28,29, the superstructures were described in terms of the unit cells of the corresponding *disordered* structures (see Sec. III above), according to the usual method of static concentration waves (e.g., Refs. 25–27). As a result, within the Brout approach, the expressions for the free energy were obtained for the disordered state, $L1_0$ and $L1_2$ structures of the fcc lattice gas. That expression for the disordered state is identical to Eq. (44) with $\mu_i=0$ and neglecting nonpair atomic interactions. The expressions for the free energy of $L1_0$ and $L1_2$ structures obtained in Refs. 28,29 are more complicated than Eq. (38). A general expression for the free energy of arbitrary superstructure was not obtained and nonpair atomic interactions were not taken into account in Refs. 28,29. Besides, the quantities such as μ_i were not introduced in Refs. 28,29 because the canonical formalism was used. Therefore, by the same line of reasoning as below in Sec. VI, one may conclude that the numerical accuracy of the

approximation obtained in Refs. 28,29 is not higher than that of the mean-field one.

It is remarkable that the Debye-Hückel approximation can be derived within the same statistical-thermodynamic approach as the ring approximation, and one can find similarities in the corresponding expressions for the free energy despite the principal difference of the simple gas and lattice-gas models (e.g., Ref. 41).

It should be noted that in fact our derivation within the ring approximation is just the different approach (within the lattice-gas model plus grand canonical formalism) to the Brout approximation elaborated in Refs. 10–12 within the Ising model (see also Ref. 36). Perhaps, one may even call the ring approximation as the Brout one. The generalization of the ring (Brout) approximation to the case of the lattice-gas model has the utility by itself. Besides, the consideration of a long-range atomic order (correspondingly, antiferromagnetic states within the Ising model), a non-Bravais crystal lattice, and nonpair interactions is much easier within our approach than in the framework of the initial Brout approach.

In our opinion, it would be interesting and helpful to compare the above-denoted approximations in more detail in a separate paper. In the present (see Sec. XIII below) and subsequent³⁶ papers we performed the detailed numerical study of just the ring approximation, which can help to understand the features of similar approximations as well.

VI. APPLICABILITY OF THE RING APPROXIMATION

As in all diagrammatic methods, we have to use not only theoretical justifications but also trial-and-error method to get analytically and/or numerically adequate results in standard cases (e.g., Ref. 33). Usually, it is not possible to derive *completely* consistent approximation without summing *all* the diagrams.⁴² Besides, the practical feasibility (e.g., the possibility of analytical summation of certain type of diagrams) plays an important role in a choice of approximation.

The first approximation we made consists in taking into account only the terms proportional to the zeroth and first powers of the quantity z^{-1} in the cumulant expansion with z being equal to the effective number of atoms interacting with one fixed atom in Brout classification^{10–12} (see also Secs. 5–7 in Ref. 17). In diagram technique language, it means that we include into consideration the infinite number of the ring-type diagrams (third column in Fig. 1). Such a “vertical” (see Fig. 1) way of diagram summation, when z^{-1} is chosen as a small parameter, is alternative to the usual “horizontal” one, when T^{-1} is chosen as a small parameter (e.g., Refs. 25,26,30,43). Note that z^{-1} expansion is referred to as high-density one in Refs. 10,11. Such a name seems not to be adequate because big values of z correspond to long-range atomic interactions rather than to high concentration of $A(B)$ -type atoms.

It should be emphasized that both classifications of the terms in the cumulant expansion by the powers of T^{-1} and z^{-1} are approximate and have only a suggestive meaning. Brout classification is not rigorous by its nature. At T^{-1} estimation we do not take into account an implicit temperature

dependence of the terms in the cumulant expansion through P_i and μ_i . Besides the numerical testing (see Sec. XIII below), the ring approximation is supported by its similarity to other approximations (see Sec. V) as well as by the fact that we obtain the high-accuracy spherical model approximation for the short-range order by the method of differentiation with respect to potential within the ring approximation (see Sec. IX below). As it was pointed out in Sec. 11 of Ref. 33, the more the contribution from a vertex, the less the lines enter a vertex of a diagram. Thus, one may expect that the ring diagrams, for which only two lines enter each vertex, mainly contribute to the cumulant expansion. If the Brout classification is valid, one should expect an increase of the numerical accuracy of the ring approximation with increase of the radius of atomic interactions and/or of the dimensionality of the crystal lattice because the parameter z^{-1} decreases in such cases. Note that one may consider the quantity z as the effective dimensionality of the Hamiltonian (see Sec. 1.6 in Ref. 44).

The second approximation we made consists in a neglect of the terms corresponding to the *reducible* diagrams in the cumulant expansion. [Note that some of the reducible diagrams are implicitly taken into account by the renormalization (28) of the diagram vertices, see below.] The account of such terms is problematic in practice. There is a number of prerequisites to neglect such terms^{15,25,26,32,43} but the ultimate answer seems to be obtained only through the numerical calculations. The neglect of the reducible diagrams corresponding to the low powers of T^{-1} can result, for example, in the low numerical accuracy of the ring approximation at sufficiently low temperatures when the contribution of such diagrams can be considerable. Besides, the results of the ring approximation can be inadequate in the immediate vicinity of the critical temperatures (and concentrations) of the absolute instability of structures, where the contribution from the divergent reducible diagrams [and those irreducible that are proportional to z^{-n} ($n > 1$)] is considerable (see Chap. 2, Sec. 6 in Ref. 12). Thus, we should expect the low numerical accuracy at calculation of the temperatures of phase transformations of the second or close to second orders, when the interval between the critical temperature of the absolute instability and that of the phase transformation is comparatively small (or vanishes).

We describe our system within the grand canonical ensemble. The necessity of use of such an ensemble is caused by our use of the transformation

$$\langle C_{i_1, \mathbf{R}_1} C_{i_2, \mathbf{R}_2} \cdots C_{i_n, \mathbf{R}_n} \rangle = \langle C_{i_1, \mathbf{R}_1} \rangle \langle C_{i_2, \mathbf{R}_2} \rangle \cdots \langle C_{i_n, \mathbf{R}_n} \rangle \quad (48)$$

[$n > 1$, $(i_l, \mathbf{R}_l) \neq (i_m, \mathbf{R}_m)$] in all the cumulant expansion terms. In the case of the *canonical* ensemble, the transformation (48) is valid for only *finite* values of n , when the fixed concentration restriction on summation over the configurational states is negligible in thermodynamic limit. Thus, if we take into account the terms that include quantities $\langle C_{i_1, \mathbf{R}_1} C_{i_2, \mathbf{R}_2} \cdots C_{i_n, \mathbf{R}_n} \rangle$ with only *finite* values of n , it is correct to use the *canonical* ensemble. This is the case of high-temperature approximations of finite orders as well as

of MF approximation (see Sec. IV A). However, if we take into account the terms that include quantities $\langle C_{i_1, \mathbf{R}_1} C_{i_2, \mathbf{R}_2} \cdots C_{i_n, \mathbf{R}_n} \rangle$ with *infinite* values of n (just like in the ring approximation), for correctness of the transformation (48) we have to use the grand canonical ensemble. The necessity to change the statistical ensemble was discussed, e.g., in Sec. 4.3 of Ref. 45.

From Eq. (43), it follows that within the MF approximation the critical temperature T_c^{MF} of the absolute instability of the disordered state is determined as [see Eq. (2.3) in Ref. 46]

$$k_B T_c^{\text{MF}} = -c(1-c) \min_{\mathbf{k}} \bar{\Phi}_{\mathbf{k}}^{(2)} = -c(1-c) \bar{\Phi}_{\mathbf{k}_0}^{(2)}. \quad (49)$$

Let us put $\mu = 0$ in Eq. (44) for a moment, what is the same as consideration within the canonical ensemble (see Sec. III). In such a case, due to the presence of the logarithm, the free energy (44) of the disordered lattice gas does not exist at $T \leq T_c^{\text{MF}}$, even within the ring approximation. Correspondingly, the critical temperature of the absolute instability of the disordered state as well as the order-disorder phase transition temperature can be only more or equal to T_c^{MF} . Thus, we arrive at the important conclusion that without the grand canonical consideration (i.e., without introduction of μ), even taking into account the ring diagrams in cumulant expansion, it is impossible to diminish the (usually too high) order-disorder phase-transition temperature obtained within the MF approximation. In Sec. XIII below, it is shown that the use of the ring approximation within the *grand* canonical formalism allows to substantially increase the numerical accuracy of the MF approximation results. There is a number of other important discrepancies within the ring approximation in the canonical formalism.^{10-12,33,42}

In order to get the high-accuracy results within the ring approximation it is important to introduce μ_i into the $W_{i_1, \mathbf{R}_1; i_2, \mathbf{R}_2}^{(2)}$ [see Eq. (8)] *before* the classification of the terms of the cumulant expansion in powers of z^{-1} . The quantities analogous to our μ_i were introduced on several grounds within a number of approximations (see Sec. V). The possibility to get the results within the *grand* canonical formalism that are different from those obtained within the canonical formalism was pointed out in Sec. 2.3 of Ref. 14.

In order to obtain the physical adequacy and high numerical accuracy, we have also introduced the self-consistent field approximation (28). As a result, if we put $\mu_i = 0$ we get the adequate transformation of our final expressions to those obtained within the canonical formalism. Besides, we obtain a similarity with other approximations (see Sec. V). The approximation (28) corresponds to a renormalization of the diagram vertices, i.e., to the implicit summation of additional reducible diagrams in the cumulant expansion (see Refs. 33,42 and Chap. 2, Sec. 6 in Ref. 12). Note that it is important to introduce the approximation (28) *after* the decoupling (48) because otherwise we return to the canonical consideration. We should expect the contribution of the self-consistent field approximation to the low numerical accuracy of the ring approximation within the critical regions of phase diagram. However, such a contribution must be diminished

by an increase of the radius of atomic interactions and/or of the dimensionality of the crystal lattice.

Below in Sec. XIII we will verify all the theoretical statements of the present section by numerical calculations.

VII. EQUATIONS OF STATE

The thermodynamically stable or metastable superstructures correspond, respectively, to the absolute or local minima of the free energy in the space of LRO parameters according to the variational property of the free energy (see, e.g., Sec. 4.2.2 in Ref. 14). Therefore, the values of the LRO parameters corresponding to such stable or metastable structures must satisfy the equations that follow from the condition of zero values of the first derivatives of the free energy with respect to such parameters. The present section will be devoted to a general derivation of such equations, which we shall call as the equations of state. Below in the present paper, we neglect a dependence of the mixing potentials on the quantities P_i .

A. Ring approximation

Let us consider the fluctuations $\delta P_{i,\mathbf{R}}$ of the quantities P_i . The presence of the argument \mathbf{R} in $\delta P_{i,\mathbf{R}}$ means that we take into account not only the fluctuations of the differences $P_i - P_j$ ($i \neq j$) but also the fluctuations of P_i within each sublattice. We have also to take into account the corresponding chemical potential fluctuations $\delta \mu_{i,\mathbf{R}}$ of the quantities μ_i (see Ref. 18). It is easy to show that within the ring approximation the free energy functional $f_{\text{ring}}^{\text{fluct}}$ of the fluctuating $P_{i,\mathbf{R}}$ and $\mu_{i,\mathbf{R}}$ has the following form:

$$\begin{aligned}
f_{\text{ring}}^{\text{fluct}} = & v_0 - \frac{1}{2N} \sum_i \sum_{\mathbf{R}} \mu_{i,\mathbf{R}} P_{i,\mathbf{R}} (1 - P_{i,\mathbf{R}}) \\
& + N^{-1} \sum_i \sum_{\mathbf{R}} P_{i,\mathbf{R}} V_i^{(1)} \\
& + \frac{1}{N} \sum_{n=2}^{N\nu} \frac{1}{n!} \sum_{i_1, i_2, \dots, i_n} \sum_{\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_n} \\
& \times V_{i_1, \mathbf{R}_1; i_2, \mathbf{R}_2; \dots; i_n, \mathbf{R}_n}^{(n)} P_{i_1, \mathbf{R}_1} P_{i_2, \mathbf{R}_2} \dots P_{i_n, \mathbf{R}_n} \\
& + N^{-1} k_B T \sum_i \sum_{\mathbf{R}} [P_{i,\mathbf{R}} \ln P_{i,\mathbf{R}} + (1 - P_{i,\mathbf{R}}) \ln(1 - P_{i,\mathbf{R}})] \\
& - \frac{k_B T}{2N} \sum_{n=1}^{\infty} \frac{1}{n} \sum_{i_1, i_2, \dots, i_n} \sum_{\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_n} f_{i_1, \mathbf{R}_1; i_2, \mathbf{R}_2}^{\text{fluct}} \\
& \times f_{i_2, \mathbf{R}_2; i_3, \mathbf{R}_3}^{\text{fluct}} \dots f_{i_n, \mathbf{R}_n; i_1, \mathbf{R}_1}^{\text{fluct}} \quad (50)
\end{aligned}$$

[compare with Eqs. (17), (23), and (24)], where

$$P_{i,\mathbf{R}} = P_i + \delta P_{i,\mathbf{R}}, \quad \mu_{i,\mathbf{R}} = \mu_i + \delta \mu_{i,\mathbf{R}}, \quad (51)$$

$$\begin{aligned}
f_{i_1, \mathbf{R}_1; i_m, \mathbf{R}_m}^{\text{fluct}} = & -(k_B T)^{-1} \sqrt{P_{i_1, \mathbf{R}_1} (1 - P_{i_1, \mathbf{R}_1})} \\
& \times (\mu_{i_1, \mathbf{R}_1} \delta_{i_1, i_m} \delta_{\mathbf{R}_1, \mathbf{R}_m} + \Phi_{i_1, \mathbf{R}_1; i_m, \mathbf{R}_m}^{\text{fluct}}) \\
& \times \sqrt{P_{i_m, \mathbf{R}_m} (1 - P_{i_m, \mathbf{R}_m})}, \quad (52)
\end{aligned}$$

$$\begin{aligned}
\Phi_{i_1, \mathbf{R}_1; i_m, \mathbf{R}_m}^{\text{fluct}} = & \sum_{t=0}^{N\nu-2} \frac{1}{t!} \sum_{i'_1, i'_2, \dots, i'_t} \sum_{\mathbf{R}'_1, \mathbf{R}'_2, \dots, \mathbf{R}'_t} P_{i'_1, \mathbf{R}'_1} P_{i'_2, \mathbf{R}'_2} \dots \\
& \times P_{i'_t, \mathbf{R}'_t} V_{i'_1, \mathbf{R}'_1; i'_2, \mathbf{R}'_2; \dots; i'_t, \mathbf{R}'_t; i_1, \mathbf{R}_1; i_m, \mathbf{R}_m}^{(2+t)} \quad (53)
\end{aligned}$$

[compare with Eqs. (26) and (27)] and $\mu_{i,\mathbf{R}}$ are to be determined from the equations ($i = 1, 2, \dots, \nu$)

$$\partial f_{\text{ring}}^{\text{fluct}} / \partial \mu_{i,\mathbf{R}} = 0 \quad (54)$$

[compare with Eq. (20)].

Note that the expression (50) is analogous to Eq. (7.4) in Ref. 17. The principal difference between them lies in the fact that in the present paper we consider the fluctuations of the initially LRO state rather than those of the initially disordered (i.e., without a LRO) state.

Using Eq. (54), we have for the free energy variation of the first order

$$\delta f_{\text{ring}}^{\text{fluct}} = \sum_i \sum_{\mathbf{R}} \left. \frac{\partial f_{\text{ring}}^{\text{fluct}}}{\partial P_{i,\mathbf{R}}} \right|_0 \delta P_{i,\mathbf{R}}. \quad (55)$$

In Eq. (55) and below, index 0 means that the derivatives are taken at $P_{i,\mathbf{R}} = P_i$ and $\mu_{i,\mathbf{R}} = \mu_i$:

$$\dots|_0 \equiv \dots|_{P_{i,\mathbf{R}}=P_i, \mu_{i,\mathbf{R}}=\mu_i}. \quad (56)$$

Substituting Eq. (50) into Eq. (55), we get

$$\delta f_{\text{ring}}^{\text{fluct}} = \sum_i D_i^{\text{ring}} \delta \tilde{P}_{i,0}, \quad (57)$$

where $\delta \tilde{P}_{i,\mathbf{k}}$ is the Fourier transform of $\delta P_{i,\mathbf{R}}$,

$$\delta P_{i,\mathbf{R}} = \sum_{\mathbf{k}} \delta \tilde{P}_{i,\mathbf{k}} \exp(-i\mathbf{k}\mathbf{R}), \quad (58)$$

$$\begin{aligned}
D_i^{\text{ring}} = & \tilde{\Phi}_i^{(1)} - \frac{\mu_i}{2} (1 - 2P_i) + k_B T \ln \frac{P_i}{1 - P_i} \\
& - \frac{k_B T}{2N} \sum_{\mathbf{q}} \sum_{j,l} \frac{\tilde{f}_{i,0;j,\mathbf{q};l}^{(3)} \|A_{\mathbf{q}}^{-1}\|_{lj}}{\sqrt{P_i(1 - P_i)}}, \quad (59)
\end{aligned}$$

$$\tilde{f}_{i_1, \mathbf{k}_1; i_2, \mathbf{k}_2; i_3}^{(3)} = - \frac{\prod_{m=1}^3 \sqrt{P_{i_m} (1 - P_{i_m})}}{k_B T} \tilde{\Phi}_{i_1, \mathbf{k}_1; i_2, \mathbf{k}_2; i_3}^{(3)}, \quad (60)$$

the functions $\tilde{\Phi}_i^{(1)}$ and $\tilde{\Phi}_{i_1, \mathbf{k}_1; i_2, \mathbf{k}_2; i_3}^{(3)}$ correspond to the particular cases $n=1$ and $n=3$ [see Eqs. (B2) and (B4) in

Appendix B], respectively, of the function $\tilde{\Phi}_{i_1, \mathbf{k}_1; i_2, \mathbf{k}_2; \dots; i_{n-1}, \mathbf{k}_{n-1}; i_n}^{(n)}$ defined in Eq. (34).

Taking into account the constraint for $P_{i, \mathbf{R}}$

$$\sum_{i=1}^{\nu} \sum_{\mathbf{R}} P_{i, \mathbf{R}} = \langle N_A \rangle \quad (61)$$

(N_A is the total number of A-type atoms) and correspondingly for $\delta P_{i, \mathbf{R}}$ and $\delta \tilde{P}_{i, \mathbf{k}}$

$$\sum_{i=1}^{\nu} \sum_{\mathbf{R}} \delta P_{i, \mathbf{R}} = N \sum_{i=1}^{\nu} \delta \tilde{P}_{i, \mathbf{0}} = 0, \quad (62)$$

we can express $\delta \tilde{P}_{\nu, \mathbf{0}}$ as

$$\delta \tilde{P}_{\nu, \mathbf{0}} = - \sum_{i=1}^{\nu-1} \delta \tilde{P}_{i, \mathbf{0}}. \quad (63)$$

Substituting Eq. (63) into Eq. (57), we obtain the expression for $\delta f_{\text{ring}}^{\text{fluct}}$ through the *independent* fluctuations

$$\delta f_{\text{ring}}^{\text{fluct}} = \sum_{i=1}^{\nu-1} (D_i^{\text{ring}} - D_{\nu}^{\text{ring}}) \delta \tilde{P}_{i, \mathbf{0}}. \quad (64)$$

Because the free energy variation of the first-order $\delta f_{\text{ring}}^{\text{fluct}}$ vanishes in case of thermodynamically stable or metastable superstructures:

$$\delta f_{\text{ring}}^{\text{fluct}} = 0, \quad (65)$$

from Eq. (64) we obtain the following equations of state ($i = 1, 2, \dots, \nu-1$):³⁵

$$\{D_i^{\text{ring}} - D_{\nu}^{\text{ring}} = 0, \quad (66)$$

where D_i^{ring} is defined in Eq. (59). Note that, at neglect of the nonpair interactions, the obtained equations of state are similar to the corresponding ones derived within the Onsager cavity-field approximation.^{24,37,38}

As an example, let us write down the equations of state for $L1_0$ and $L1_2$ structures in case of presence of only nearest-neighbor pair atomic interactions $V_{i=1}^{(2)}$:

$$\begin{aligned} k_B T \ln \frac{P_2(1-P_1)}{P_1(1-P_2)} + \frac{1}{2} [-\mu_1(1-2P_1) + \mu_2(1-2P_2)] \\ = -4V_{i=1}^{(2)} \eta, \end{aligned} \quad (67)$$

where the corresponding P_i and LRO parameter η are related below in Eqs. (132) and (133) and μ_i are to be determined from Eq. (39). Note that the difference between Eq. (67) and the corresponding expressions obtained within the MF approximation [e.g., Eqs. (16.8) and (16.24) in Ref. 9] lies in the nonzero value of the quantities μ_i .

Case of the almost maximum LRO parameter

In wide temperature-concentration intervals (not only at low temperatures), the differences between the values of the LRO parameters and their maximum possible values are small. Thus, within such intervals, the general equations of

state (66) can be simplified by series expansion in powers of such small differences with taking into account only lowest powers.

Let us consider the case of structures characterized by one LRO parameter η . In this case, all the quantities P_i ($i = 1, 2, \dots, \nu$) take only two different values P_I and P_{II} (e.g., Sec. 1 in Ref. 9),

$$P_I = c + (1 - c_{\text{st}}) \eta, \quad P_{II} = c - c_{\text{st}} \eta, \quad (68)$$

where c_{st} is the stoichiometric concentration of the structure. The maximum values of η, P_I, P_{II} ($\eta_{\text{max}}, P_I^{\text{max}}, P_{II}^{\text{max}}$, respectively) possible at a given concentration c are the following:

$$\begin{aligned} \eta_{\text{max}} = \frac{c}{c_{\text{st}}}, \quad P_I^{\text{max}} = \frac{c}{c_{\text{st}}}, \quad P_{II}^{\text{max}} = 0 \quad (c \leq c_{\text{st}}), \\ \eta_{\text{max}} = \frac{1-c}{1-c_{\text{st}}}, \quad P_I^{\text{max}} = 1, \quad P_{II}^{\text{max}} = \frac{c-c_{\text{st}}}{1-c_{\text{st}}} \quad (c > c_{\text{st}}). \end{aligned} \quad (69)$$

From Eq. (66), assuming that $\eta \approx \eta_{\text{max}}$, we obtain

$$\eta = \frac{c}{c_{\text{st}}} \left[1 - \frac{1}{1 + (c_{\text{st}} - c)(\varepsilon - 1)} \right] \quad (c < c_{\text{st}}), \quad (70)$$

$$\eta = 1 - \frac{-1 + \sqrt{1 + 4c_{\text{st}}(1 - c_{\text{st}})(\varepsilon^{-1} - 1)}}{2c_{\text{st}}(1 - c_{\text{st}})(\varepsilon^{-1} - 1)} \quad (c = c_{\text{st}} \leq 0.5), \quad (71)$$

$$\eta = 1 - \frac{-1 + \sqrt{1 + 4c_{\text{st}}(1 - c_{\text{st}})(\varepsilon - 1)}}{2c_{\text{st}}(1 - c_{\text{st}})(\varepsilon - 1)} \quad (c = c_{\text{st}} > 0.5), \quad (72)$$

$$\eta = \frac{1-c}{1-c_{\text{st}}} \left[1 - \frac{1}{1 + (c - c_{\text{st}})(\varepsilon - 1)} \right] \quad (c > c_{\text{st}}), \quad (73)$$

where

$$\varepsilon = \exp\{(k_B T)^{-1} [R_{i=II}(\{P_j^{\text{max}}\}) - R_{i=I}(\{P_j^{\text{max}}\})]\}, \quad (74)$$

$$R_i(\{P_j\}) = \tilde{\Phi}_i^{(1)} - \frac{1}{2} \mu_i (1 - 2P_i)$$

$$- \frac{k_B T}{2N} \sum_{\mathbf{q}} \sum_{j, l} \frac{\tilde{f}_{i, \mathbf{0}; j, \mathbf{q}; l}^{(3)} \|A_{\mathbf{q}}^{-1}\|_{lj}}{\sqrt{P_i(1-P_i)}}. \quad (75)$$

Note that $R_{i=I}(\{P_j^{\text{max}}\})$ means that i is equal to the number of any sublattice of type I and that we put $P_j = P_j^{\text{max}}$ ($j = 1, 2, \dots, \nu$). The quantities μ_i ($i = 1, 2, \dots, \nu$) are to be determined from Eq. (39). It should be emphasized that the condition of $T \rightarrow 0$ was not imposed at derivation of Eqs. (70)–(75), so that they could not be applied only at low temperatures.

The expressions (70)–(75) were used at our calculation of the phase diagrams below Sec. XIII. Especially, they proved to be useful at low temperatures when the difference between

the value of the LRO parameter and its maximum possible value is of the same order as the precision of the computer calculations.

B. Mean-field (MF) approximation

Using Eq. (35), within the MF approximation we obtain the following free energy functional $f_{\text{MF}}^{\text{fluct}}$ of the fluctuating $P_{i,\mathbf{R}}$:

$$\begin{aligned} f_{\text{MF}}^{\text{fluct}} = & v_0 + N^{-1} \sum_i \sum_{\mathbf{R}} P_{i,\mathbf{R}} V_i^{(1)} \\ & + \frac{1}{N} \sum_{n=2}^{N\nu} \frac{1}{n!} \sum_{i_1, i_2, \dots, i_n} \sum_{\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_n} \\ & \times V_{i_1, \mathbf{R}_1; i_2, \mathbf{R}_2; \dots; i_n, \mathbf{R}_n}^{(n)} P_{i_1, \mathbf{R}_1} P_{i_2, \mathbf{R}_2} \dots P_{i_n, \mathbf{R}_n} \\ & + N^{-1} k_B T \sum_i \sum_{\mathbf{R}} [P_{i,\mathbf{R}} \ln P_{i,\mathbf{R}} + (1 - P_{i,\mathbf{R}}) \ln(1 - P_{i,\mathbf{R}})]. \end{aligned} \quad (76)$$

By the same way as in the preceding section, we arrive at the following free energy variation of the first order:

$$\begin{aligned} \delta f_{\text{MF}}^{\text{fluct}} = & \sum_i \sum_{\mathbf{R}} \left. \frac{\partial f_{\text{MF}}^{\text{fluct}}}{\partial P_{i,\mathbf{R}}} \right|_{P_{i,\mathbf{R}}=P_i} \delta P_{i,\mathbf{R}} \\ = & \sum_{i=1}^{\nu-1} (D_i^{\text{MF}} - D_\nu^{\text{MF}}) \delta \tilde{P}_{i,0}, \end{aligned} \quad (77)$$

where

$$D_i^{\text{MF}} = \tilde{\Phi}_i^{(1)} + k_B T \ln \frac{P_i}{1 - P_i} \quad (78)$$

[the function $\tilde{\Phi}_i^{(1)}$ is defined in Eq. (B2)]. Correspondingly, the equations of state have the following form ($i = 1, 2, \dots, \nu - 1$):

$$\{D_i^{\text{MF}} - D_\nu^{\text{MF}} = 0. \quad (79)$$

From comparison of Eqs. (59) and (78) it follows that one can transform the equations of state obtained within the ring approximation to those of the MF approximation one by putting $\mu_i = 0$ and neglecting the last term in Eq. (59). Note that the last term in Eq. (59) gives contribution only in case of presence of nonpair atomic interactions.

Equations of state (79) are the generalization of those presented in Eq. (5) of Ref. 22 to the case of presence of nonpair atomic interactions of any order. Besides, we take into account the constraint (61) explicitly, instead of introduction of the Lagrange multiplier as it was done in Ref. 22 (in spirit of Khachatryan approach²⁵⁻²⁷).

In the case of almost maximum LRO parameter, within the MF approximation from Eq. (79) we obtain the same expressions (70)–(73) but with

$$\varepsilon = \exp\{(k_B T)^{-1} [\tilde{\Phi}_{i=\Pi}^{(1)}(\{P_j^{\text{max}}\}) - \tilde{\Phi}_{i=1}^{(1)}(\{P_j^{\text{max}}\})]\}. \quad (80)$$

Note that the expression (71) [taking into account Eq. (80)] transforms into Eq. (19.13) in Ref. 9 if one additionally imposes the condition of $T \rightarrow 0$ and neglects all nonpair atomic interactions. The expressions (70)–(75) together with Eq. (80) were used at our calculations of the phase diagrams within the MF approximation in Sec. XIII below.

VIII. STRUCTURAL STABILITY

The condition (65) of the thermodynamical stability or metastability of the superstructures is the necessary condition. In order to study the sufficient condition we have to consider the free energy variation of the second order.

A. Ring approximation

Within the ring approximation the free energy variation of the second-order $\delta^2 f_{\text{ring}}^{\text{fluct}}$ has the following form:

$$\begin{aligned} \delta^2 f_{\text{ring}}^{\text{fluct}} = & \frac{1}{2} \sum_{i,j} \sum_{\mathbf{R}_1, \mathbf{R}_2} \left[\left. \frac{\partial^2 f_{\text{ring}}^{\text{fluct}}}{\partial P_{i,\mathbf{R}_1} \partial P_{j,\mathbf{R}_2}} \right|_0 \delta P_{i,\mathbf{R}_1} \delta P_{j,\mathbf{R}_2} \right. \\ & + \left. \frac{2 \partial^2 f_{\text{ring}}^{\text{fluct}}}{\partial P_{i,\mathbf{R}_1} \partial \mu_{j,\mathbf{R}_2}} \right|_0 \delta P_{i,\mathbf{R}_1} \delta \mu_{j,\mathbf{R}_2} \\ & + \left. \frac{\partial^2 f_{\text{ring}}^{\text{fluct}}}{\partial \mu_{i,\mathbf{R}_1} \partial \mu_{j,\mathbf{R}_2}} \right|_0 \delta \mu_{i,\mathbf{R}_1} \delta \mu_{j,\mathbf{R}_2} \Big]. \end{aligned} \quad (81)$$

From Eq. (54), by taking the first derivative with respect to $P_{i,\mathbf{R}}$, one can obtain that

$$\begin{aligned} \frac{d}{dP_{i,\mathbf{R}_1}} \frac{\partial F}{\partial \mu_{j,\mathbf{R}_2}} = & \frac{\partial^2 F}{\partial P_{i,\mathbf{R}_1} \partial \mu_{j,\mathbf{R}_2}} \\ & + \sum_l \sum_{\mathbf{R}'} \frac{\partial^2 F}{\partial \mu_{l,\mathbf{R}'} \partial \mu_{j,\mathbf{R}_2}} \frac{\partial \mu_{l,\mathbf{R}'}}{\partial P_{i,\mathbf{R}_1}} = 0. \end{aligned} \quad (82)$$

Besides, for the variation $\delta \mu_{i,\mathbf{R}}$, we generally have up to the second order

$$\begin{aligned} \delta \mu_{i,\mathbf{R}} = & \sum_j \sum_{\mathbf{R}_1} \frac{\partial \mu_{i,\mathbf{R}}}{\partial P_{j,\mathbf{R}_1}} \delta P_{j,\mathbf{R}_1} \\ & + \frac{1}{2} \sum_{j,l} \sum_{\mathbf{R}_1, \mathbf{R}_2} \frac{\partial^2 \mu_{i,\mathbf{R}}}{\partial P_{j,\mathbf{R}_1} \partial P_{l,\mathbf{R}_2}} \delta P_{j,\mathbf{R}_1} \delta P_{l,\mathbf{R}_2}. \end{aligned} \quad (83)$$

Thus, from Eq. (81), taken into account Eqs. (82) and (83), we get up to the second order

$$\delta^2 f_{\text{ring}}^{\text{fluct}} = \frac{1}{2} \sum_{i,j} \sum_{\mathbf{R}_1, \mathbf{R}_2} \delta P_{i, \mathbf{R}_1} \delta P_{j, \mathbf{R}_2} \left[\frac{\partial^2 f_{\text{ring}}^{\text{fluct}}}{\partial P_{i, \mathbf{R}_1} \partial P_{j, \mathbf{R}_2}} + \sum_{\mathbf{R}'} \sum_{\mathbf{R}''} \frac{\partial^2 f_{\text{ring}}^{\text{fluct}}}{\partial P_{i, \mathbf{R}_1} \partial \mu_{l, \mathbf{R}'}} \frac{\partial \mu_{l, \mathbf{R}''}}{\partial P_{j, \mathbf{R}_2}} \right]. \quad (84)$$

Substituting $f_{\text{ring}}^{\text{fluct}}$ from Eq. (50) into Eq. (84), we obtain (see the details of derivation in Appendix C)

$$\delta^2 f_{\text{ring}}^{\text{fluct}} = \frac{k_B T}{2} \sum_{i,j} \sum_{\mathbf{k}} \beta_{i,j,\mathbf{k}}^{\text{ring}} \delta \tilde{P}_{j,\mathbf{k}}^* \delta \tilde{P}'_{i,\mathbf{k}}, \quad (85)$$

where

$$\delta \tilde{P}'_{i,\mathbf{k}} = \frac{\delta \tilde{P}_{i,\mathbf{k}}}{\sqrt{P_i(1-P_i)}}, \quad (86)$$

$$\begin{aligned} \beta_{i,j,\mathbf{k}}^{\text{ring}} = & A_{\mathbf{k}}^{ij} + \frac{1}{2} \frac{1-2P_i}{\sqrt{P_i(1-P_i)}} \left[\|I_{\mathbf{k}}^{-1}\|_{ij} - \delta_{ij} \right] \frac{1-2P_j}{\sqrt{P_j(1-P_j)}} \\ & + \sum_{l,s} T_{\mathbf{k}}^{il} \|I_{\mathbf{k}}^{-1}\|_{ls} \left[\frac{1}{2} T_{-\mathbf{k}}^{js} - \frac{1-2P_j}{\sqrt{P_j(1-P_j)}} \delta_{sj} \right] \\ & - \frac{1}{2N} \sum_{i_1, i_2} \sum_{\mathbf{q}} \tilde{f}_{i_1, \mathbf{k}; j, -\mathbf{k}; i_1, \mathbf{q}; i_2}^{(4)} \|A_{\mathbf{q}}^{-1}\|_{i_2, i_1} \\ & - \frac{1}{2N} \sum_{i_1, i_2, i_3, i_4} \sum_{\mathbf{q}} \tilde{f}_{i_1, \mathbf{q}; -\mathbf{k}; i_2, -\mathbf{q}; i}^{(3)} \|A_{\mathbf{q}}^{-1}\|_{i_2, i_3} \\ & \times \tilde{f}_{i_3, \mathbf{q}; i_4, \mathbf{k}; -\mathbf{q}; j}^{(3)} \|A_{-\mathbf{q}}^{-1}\|_{i_4, i_1}, \end{aligned} \quad (87)$$

the function $\tilde{f}_{i_1, \mathbf{k}_1; i_2, \mathbf{k}_2; i_3, \mathbf{k}_3; i_4}^{(3)}$ was defined in Eq. (60),

$$\begin{aligned} \tilde{f}_{i_1, \mathbf{k}_1; i_2, \mathbf{k}_2; i_3, \mathbf{k}_3; i_4}^{(4)} = & - \frac{\prod_{m=1}^4 \sqrt{P_{i_m}(1-P_{i_m})}}{k_B T} \\ & \times \tilde{\Phi}_{i_1, \mathbf{k}_1; i_2, \mathbf{k}_2; i_3, \mathbf{k}_3; i_4}^{(4)}, \end{aligned} \quad (88)$$

the function $\tilde{\Phi}_{i_1, \mathbf{k}_1; i_2, \mathbf{k}_2; i_3, \mathbf{k}_3; i_4}^{(4)}$ in Eq. (88) corresponds to the particular case $n=4$ [see Eq. (B5) in Appendix B] of the function $\tilde{\Phi}_{i_1, \mathbf{k}_1; i_2, \mathbf{k}_2; \dots; i_{n-1}, \mathbf{k}_{n-1}; i_n}^{(n)}$ defined in Eq. (34), $I_{\mathbf{k}}^{-1}$ is the matrix inverse to $I_{\mathbf{k}}$, which has the elements

$$I_{\mathbf{k}}^{ij} = N^{-1} \sum_{\mathbf{q}} \|A_{\mathbf{k}-\mathbf{q}}^{-1}\|_{ij} \|A_{\mathbf{q}}^{-1}\|_{ij}, \quad (89)$$

$$T_{\mathbf{k}}^{ij} = N^{-1} \sum_{i_1, i_2} \sum_{\mathbf{q}} \|A_{\mathbf{q}}^{-1}\|_{j i_1} \tilde{f}_{i_1, \mathbf{q}; i_2, -(\mathbf{k}+\mathbf{q}); i}^{(3)} \|A_{\mathbf{k}+\mathbf{q}}^{-1}\|_{i_2 j}. \quad (90)$$

Note that $\beta_{i,j,\mathbf{k}}^{\text{ring}}$ can be named as the inverse generalized susceptibility within the lattice-gas model (Secs. 4.2.4 and 4.3.3 in Ref. 14).

The necessary and sufficient condition of the thermodynamical stability or metastability of a superstructure is as follows:

$$\delta^2 f_{\text{ring}}^{\text{fluct}} > 0, \quad (91)$$

which [together with Eq. (65)] guarantee the presence of a local minimum of the free energy in the space of LRO parameters. Substituting Eq. (85) into Eq. (91), we obtain

$$\delta^2 f_{\text{ring}}^{\text{fluct}} = \frac{k_B T}{2} \sum_{\sigma} \sum_{\mathbf{k}} \Lambda_{\sigma, \mathbf{k}} |d_{\sigma, \mathbf{k}}|^2 > 0, \quad (92)$$

where $\Lambda_{\sigma, \mathbf{k}}$ are the eigenvalues of Hermitian matrix $\beta_{\mathbf{k}}^{\text{ring}}$ with the elements $\beta_{i,j,\mathbf{k}}^{\text{ring}}$,

$$\sum_j \beta_{i,j,\mathbf{k}}^{\text{ring}} v_{\sigma, \mathbf{k}}^j = \Lambda_{\sigma, \mathbf{k}} v_{\sigma, \mathbf{k}}^i \Leftrightarrow \beta_{\mathbf{k}}^{\text{ring}} \mathbf{v}_{\sigma, \mathbf{k}} = \Lambda_{\sigma, \mathbf{k}} \mathbf{v}_{\sigma, \mathbf{k}}, \quad (93)$$

$v_{\sigma, \mathbf{k}}^i$ are the components of the eigenvectors $\mathbf{v}_{\sigma, \mathbf{k}}$ of the matrix $\beta_{\mathbf{k}}^{\text{ring}}$,

$$\mathbf{v}_{\sigma_1, \mathbf{k}} \mathbf{v}_{\sigma_2, \mathbf{k}} = \delta_{\sigma_1, \sigma_2}, \quad \sum_{\sigma} v_{\sigma, \mathbf{k}}^i v_{\sigma, \mathbf{k}}^j = \delta_{ij}, \quad (94)$$

$d_{\sigma, \mathbf{k}}$ are the coordinates of the vectors $\delta \tilde{\mathbf{P}}'_{\mathbf{k}}$ (with the elements $\delta \tilde{P}'_{i,\mathbf{k}}$) in the complete space of the eigenvectors $\mathbf{v}_{\sigma, \mathbf{k}}$

$$\delta \tilde{\mathbf{P}}'_{i,\mathbf{k}} = \sum_{\sigma} d_{\sigma, \mathbf{k}} v_{\sigma, \mathbf{k}}^i \Leftrightarrow \delta \tilde{\mathbf{P}}'_{\mathbf{k}} = \sum_{\sigma} d_{\sigma, \mathbf{k}} \mathbf{v}_{\sigma, \mathbf{k}}. \quad (95)$$

Because the condition (92) must be valid for any values of $\delta \tilde{\mathbf{P}}'_{\mathbf{k}}$ (and correspondingly of $d_{\sigma, \mathbf{k}}$), we get the following necessary and sufficient condition of the thermodynamical stability or metastability of a superstructure [together with Eq. (66)]:

$$\Lambda_{\sigma, \mathbf{k}} > 0 \quad (96)$$

(for any σ and \mathbf{k}). The critical temperature T_c of the absolute instability of a superstructure is determined by the equation³⁵

$$\min_{\sigma, \mathbf{k}} \Lambda_{\sigma, \mathbf{k}} = \Lambda_{\sigma_0, \mathbf{k}_0} = 0 \Leftrightarrow \det \beta_{\mathbf{k}}^{\text{ring}} = 0, \quad (97)$$

where σ_0 and \mathbf{k}_0 may be called the instability mode and wave vector, respectively, $\det \beta_{\mathbf{k}}^{\text{ring}}$ is the determinant of the matrix $\beta_{\mathbf{k}}^{\text{ring}}$ with the elements defined in Eq. (87). The important feature of the ring approximation (which is absent within the MF one) is that the wave vector \mathbf{k}_0 of instability of the same superstructure can be different for different concentrations of the lattice gas even in the case of constant and pair atomic interactions (see examples below in Sec. XIII).

1. Orientational order

The instability mode σ_0 and wave vector \mathbf{k}_0 contain the important information about the thermodynamically stable structure to appear after the corresponding phase transformation from a given structure (see below Sec. X). However, both cases of decomposition (segregation) and orientational order correspond to $\mathbf{k}_0 = \mathbf{0}$, where by the orientational order

we mean the redistribution of probabilities P_i among the same sublattices without a change of the primitive unit cell. In order to distinguish between the decomposition and orientational order, let us consider the fluctuations $\delta\tilde{P}_{i,\mathbf{k}=\mathbf{0}}$, implying the constraint (63),

$$\begin{aligned}\delta^2 f_{\text{ring}}^{\text{fluct}} &= \frac{k_B T}{2} \sum_{i,j=1}^{\nu} B_{i,j,\mathbf{0}}^{\text{ring}} \delta\tilde{P}_{j,\mathbf{0}}^* \delta\tilde{P}_{i,\mathbf{0}} \\ &\stackrel{\text{Eq. (63)}}{=} \frac{k_B T}{2} \sum_{i,t=1}^{\nu-1} D_{i,t,\mathbf{0}}^{\text{ring}} \delta\tilde{P}_{t,\mathbf{0}}^* \delta\tilde{P}_{i,\mathbf{0}},\end{aligned}\quad (98)$$

where

$$B_{i,j,\mathbf{k}}^{\text{ring}} = \frac{\beta_{i,j,\mathbf{k}}^{\text{ring}}}{\sqrt{P_i(1-P_i)P_j(1-P_j)}}, \quad (99)$$

$$D_{i,t,\mathbf{0}}^{\text{ring}} = B_{i,t,\mathbf{0}}^{\text{ring}} - B_{i,\nu,\mathbf{0}}^{\text{ring}} - B_{\nu,t,\mathbf{0}}^{\text{ring}} + B_{\nu,\nu,\mathbf{0}}^{\text{ring}}. \quad (100)$$

The quantity $\delta^2 f_{\text{ring}}^{\text{fluct}}$ in Eq. (98) contains only the fluctuations corresponding to the orientational order because the implied constraint (63) means that the total concentrations of the atoms of all types are fixed. (In case of decomposition those concentrations change.)

Thus, if from Eq. (97) we have found that the instability wave vector $\mathbf{k}_0 = \mathbf{0}$, we have to study the eigenvalues of the matrix $D_{\mathbf{0}}^{\text{ring}}$ with the elements determined in Eq. (100). In the case of decomposition all such eigenvalues are positive and any negative eigenvalue indicates the orientational order.

2. Case of the disordered lattice gas with a Bravais crystal lattice

Let us consider a particular case of the disordered two-component lattice gas with a Bravais crystal lattice, which is important from a practical point of view. In this case it is not necessary to introduce the sublattice index i and instead of Eq. (85) we have

$$\delta^2 f_{\text{ring}}^{\text{fluct}} = \frac{k_B T}{2c(1-c)} \sum_{\mathbf{k}} \beta_{\mathbf{k}}^{\text{ring}} |\delta\tilde{P}_{\mathbf{k}}|^2, \quad (101)$$

where

$$\begin{aligned}\beta_{\mathbf{k}}^{\text{ring}} &= A_{\mathbf{k}} + \frac{(1-2c)^2}{2c(1-c)} \left[\frac{1}{I_{\mathbf{k}}} - 1 \right] + \frac{c^2(1-c)^2}{2k_B T} Q_{\mathbf{k}} \\ &+ \frac{c(1-c)}{k_B T} T_{\mathbf{k}}^{(1)} \left\{ \frac{c^2(1-c)^2}{2k_B T} \left[\frac{T_{\mathbf{k}}^{(1)}}{I_{\mathbf{k}}} - \frac{T_{\mathbf{k}}^{(2)}}{T_{\mathbf{k}}^{(1)}} \right] + \frac{1-2c}{I_{\mathbf{k}}} \right\},\end{aligned}\quad (102)$$

$$A_{\mathbf{k}} = 1 + \frac{c(1-c)}{k_B T} [\mu + \tilde{\Phi}_{\mathbf{k}}^{(2)}], \quad (103)$$

$$I_{\mathbf{k}} = \frac{1}{N} \sum_{\mathbf{q}} \frac{1}{A_{\mathbf{q}} A_{\mathbf{k}+\mathbf{q}}}, \quad Q_{\mathbf{k}} = \frac{1}{N} \sum_{\mathbf{q}} \frac{\tilde{\Phi}_{\mathbf{k},-\mathbf{k},\mathbf{q}}^{(4)}}{A_{\mathbf{q}}}, \quad (104)$$

$$T_{\mathbf{k}}^{(1)} = \frac{1}{N} \sum_{\mathbf{q}} \frac{\tilde{\Phi}_{\mathbf{q},-(\mathbf{k}+\mathbf{q})}^{(3)}}{A_{\mathbf{q}} A_{\mathbf{k}+\mathbf{q}}}, \quad T_{\mathbf{k}}^{(2)} = \frac{1}{N} \sum_{\mathbf{q}} \frac{[\tilde{\Phi}_{\mathbf{q},-(\mathbf{k}+\mathbf{q})}^{(3)}]^2}{A_{\mathbf{q}} A_{\mathbf{k}+\mathbf{q}}}, \quad (105)$$

$\tilde{\Phi}_{\mathbf{k}_1, \mathbf{k}_2, \dots, \mathbf{k}_{n-1}}^{(n)}$ and $\tilde{V}_{\mathbf{k}_1, \mathbf{k}_2, \dots, \mathbf{k}_{n-1}}^{(n)}$ are defined in Eqs. (46) and (47). Note that Eqs. (102) and (103) are the particular cases of Eqs. (87) and (33).

As it follows from Eq. (101), the critical temperature T_c of the absolute instability of a disordered state is determined by the equation

$$\min_{\mathbf{k}} \beta_{\mathbf{k}} = \beta_{\mathbf{k}_0} = 0, \quad (106)$$

which is the particular case of Eq. (97) (\mathbf{k}_0 is the instability wave vector). It should be emphasized that within the ring approximation [in contrast to the MF one—Eq. (113)] even in the case of only pair atomic interactions generally $\tilde{V}_{\mathbf{k}_0}^{(2)} \neq \min_{\mathbf{k}} \tilde{V}_{\mathbf{k}}^{(2)}$, i.e., $\tilde{V}_{\mathbf{k}}^{(2)}$ has no absolute minimum at \mathbf{k}_0 .

If nonpair atomic interactions are equal to zero (i.e., $\tilde{\Phi}_{\mathbf{k}}^{(2)} = \tilde{V}_{\mathbf{k}}^{(2)}$, $T_{\mathbf{k}}^{(1)} = T_{\mathbf{k}}^{(2)} = Q_{\mathbf{k}} = 0$) and $c = 0.5$, then from Eq. (106) we obtain the familiar result¹²

$$\frac{1}{k_B T_c} = \frac{4}{N} \sum_{\mathbf{k}} [\tilde{V}_{\mathbf{k}}^{(2)} - \tilde{V}_{\mathbf{k}_0}^{(2)}]^{-1}. \quad (107)$$

B. Mean-field approximation

Within the MF approximation, using Eq. (76), we obtain the following expression for the free energy variation of the second-order $\delta^2 f_{\text{MF}}^{\text{fluct}}$:

$$\delta^2 f_{\text{MF}}^{\text{fluct}} = \frac{k_B T}{2} \sum_{i,j} \sum_{\mathbf{k}} \beta_{i,j,\mathbf{k}}^{\text{MF}} \delta\tilde{P}'_{j,\mathbf{k}} \delta\tilde{P}'_{i,\mathbf{k}}, \quad (108)$$

where

$$\beta_{i,j,\mathbf{k}}^{\text{MF}} = A_{\mathbf{k}}^{ij} |_{\mu_i=0} = \delta_{ij} + \frac{\sqrt{P_i(1-P_i)} \tilde{\Phi}_{i,\mathbf{k};j}^{(2)} \sqrt{P_j(1-P_j)}}{k_B T}, \quad (109)$$

the function $\tilde{\Phi}_{i_1, \mathbf{k}; i_2}^{(2)}$ is defined by Eq. (B3) in Appendix B.

By the same way as within the ring approximation, we obtain the necessary and sufficient condition of the thermodynamical stability or metastability of a superstructure [together with Eq. (79)]

$$k_B T > -\lambda_{\sigma, \mathbf{k}} \quad (110)$$

(for any σ and \mathbf{k}), where $\lambda_{\sigma, \mathbf{k}}$ are the eigenvalues of Hermitian matrix with the elements $\varphi_{\mathbf{k}}^{ij}$,

$$\varphi_{\mathbf{k}}^{ij} = \sqrt{P_i(1-P_i)} \tilde{\Phi}_{i,\mathbf{k};j}^{(2)} \sqrt{P_j(1-P_j)}. \quad (111)$$

The critical temperature of the absolute instability of a superstructure is determined by the equation

$$k_B T_c = -\min_{\sigma, \mathbf{k}} \lambda_{\sigma, \mathbf{k}} = -\lambda_{\sigma_0, \mathbf{k}_0}, \quad (112)$$

where σ_0 and \mathbf{k}_0 may be called the instability mode and wave vector, respectively.

Equation (112) is the generalization of that one presented in Eq. (17) in Ref. 22 to the case of presence of nonpair atomic interactions of any order. In case of the disordered state with a complex crystal lattice and only pair atomic interactions, Eq. (112) transforms into the well-known expression for the critical temperature of the absolute instability of the disordered state obtained within the MF approximation [e.g., Eq. (3.11.22) in Ref. 27]. In case of the disordered state with a Bravais crystal lattice, Eq. (112) transforms into Eq. (2.3) of Ref. 46. And finally, in the case of the disordered state with a Bravais crystal lattice and only pair atomic interactions, Eq. (112) transforms into the classical formula [e.g., Eq. (3.7.11) in Ref. 27]

$$k_B T_c = -c(1-c) \min_{\mathbf{k}} \tilde{V}_{\mathbf{k}}^{(2)} = -c(1-c) \tilde{V}_{\mathbf{k}_0}^{(2)}. \quad (113)$$

By the same way as within the ring approximation, we obtain that if from Eq. (112) we have found that $\mathbf{k}_0 = \mathbf{0}$, then we have to study the eigenvalues of the matrix D_0^{MF} with the elements ($i, t = 1, 2, \dots, \nu - 1$)

$$D_{i,t,0}^{\text{MF}} = B_{i,t,0}^{\text{MF}} - B_{i,\nu,0}^{\text{MF}} - B_{\nu,t,0}^{\text{MF}} + B_{\nu,\nu,0}^{\text{MF}},$$

where

$$B_{i,j,\mathbf{k}}^{\text{MF}} = \frac{\beta_{i,j,\mathbf{k}}^{\text{MF}}}{\sqrt{P_i(1-P_i)P_j(1-P_j)}}. \quad (114)$$

In the case of decomposition all such eigenvalues are positive and any negative eigenvalue indicates the orientational order.

IX. SHORT-RANGE ORDER (SRO)

Let us define the SRO parameters $\alpha_{\mathbf{R}}^{ij}$ as the normalized correlation function

$$\alpha_{\mathbf{R}_1 - \mathbf{R}_2}^{i_1, i_2} = \frac{\langle (C_{i_1, \mathbf{R}_1} - P_{i_1})(C_{i_2, \mathbf{R}_2} - P_{i_2}) \rangle}{\sqrt{P_{i_1}(1-P_{i_1})P_{i_2}(1-P_{i_2})}} \quad (115)$$

with the normalization factor chosen in order to fulfill the constraint

$$\alpha_{\mathbf{R}=\mathbf{0}}^{ii} = 1. \quad (116)$$

In fact, the $\alpha_{\mathbf{R}}^{ij}$ are just the generalization of Warren-Cowley parameters⁴⁷ to the case of lattice gas with a complex crystal lattice and with a LRO. So the determined SRO parameters decrease with distance and characterize the atomic correlations *besides* the LRO. The Fourier transform $\alpha_{\mathbf{k}}^{ij}$ of $\alpha_{\mathbf{R}}^{ij}$ is defined as follows:

$$\alpha_{\mathbf{k}}^{ij} = \sum_{\mathbf{R}} \alpha_{\mathbf{R}}^{ij} \exp(-i\mathbf{k}\mathbf{R}), \quad \alpha_{\mathbf{R}}^{ij} = N^{-1} \sum_{\mathbf{k}} \alpha_{\mathbf{k}}^{ij} \exp(i\mathbf{k}\mathbf{R}). \quad (117)$$

Below we shall derive the expressions for the SRO parameters within the MF and ring approximations by two meth-

ods: method of differentiation with respect to potential and thermodynamic fluctuation method.

A. Method of differentiation with respect to potential

Within this method we use the following relationship (e.g., Ref. 2):

$$\alpha_{\mathbf{R}_1 - \mathbf{R}_2}^{i_1, i_2} = \frac{(2\partial f / \partial V_{i_1, \mathbf{R}_1}^{(2)}; i_2, \mathbf{R}_2 - P_{i_1} P_{i_2})}{\sqrt{P_{i_1}(1-P_{i_1})P_{i_2}(1-P_{i_2})}}. \quad (118)$$

Within the ring approximation substituting f_{ring} from Eq. (38) [using for convenience Eqs. (23) and (24)] into Eq. (118) and then going to the Fourier transform we obtain

$$\alpha_{\mathbf{k}}^{ij} = \|A_{\mathbf{k}}^{-1}\|_{ij}, \quad (119)$$

where $\|A_{\mathbf{k}}^{-1}\|_{ij}$ means the ij element of the matrix inverse to $A_{\mathbf{k}}$ [see Eq. (33)]. The obtained expression (119) for the Fourier transform of the SRO parameters is a generalization of the spherical model approximation [see Eqs. (4.12), (6.4), and (6.5) in Ref. 17] to the case of the lattice gas with a complex crystal lattice and with a LRO. In analogy, we shall call the obtained expression (119) as the spherical model approximation for the SRO parameters.⁴⁸ In case of the disordered state with a complex crystal lattice and only pair atomic interactions, Eq. (119) transforms into Eq. (29b) in Ref. 39.

Within the MF approximation, using Eq. (118) we obtain the trivial result

$$\alpha_{\mathbf{R}}^{i_1, i_2} = \begin{cases} 1 & \text{if } i_1 = i_2 \text{ and } \mathbf{R} = \mathbf{0} \\ 0 & \text{otherwise.} \end{cases} \quad (120)$$

B. Thermodynamic fluctuation method

In the context of the thermodynamic fluctuation method (see, e.g., Secs. 111, 116, and 146 in Ref. 31, and Ref. 49 and Sec. 25a in Ref. 4), from Eq. (85) obtained within the ring approximation, it follows that

$$\langle \delta \tilde{P}'_{i, \mathbf{k}_1}^* \delta \tilde{P}'_{j, \mathbf{k}_2} \rangle_{\text{fluct}} = N^{-1} \delta_{\mathbf{k}_1 \mathbf{k}_2} \| \beta_{\mathbf{k}_1}^{-1}(\text{ring}) \|_{ij}, \quad (121)$$

where $\langle \dots \rangle_{\text{fluct}}$ means the statistical average over the Gaussian distribution of the probabilities of fluctuations, $\| \beta_{\mathbf{k}}^{-1}(\text{ring}) \|_{ij}$ is the ij element of the matrix that is inverse to $\beta_{\mathbf{k}}^{\text{ring}}$. The SRO parameters (115) can be presented as

$$\alpha_{\mathbf{R}_1 - \mathbf{R}_2}^{i_1, i_2} = \frac{\langle \delta P_{i_1, \mathbf{R}_1} \delta P_{i_2, \mathbf{R}_2} \rangle_{\text{fluct}}}{\sqrt{P_{i_1}(1-P_{i_1})P_{i_2}(1-P_{i_2})}}. \quad (122)$$

Going in Eq. (122) to the Fourier transforms $\delta \tilde{P}_{i, \mathbf{k}}$ [see Eq. (58)] and using Eq. (121), we get

$$\alpha_{\mathbf{k}}^{ij} = \| \beta_{\mathbf{k}}^{-1}(\text{ring}) \|_{ij}. \quad (123)$$

We shall call the obtained expression (123) as the ring approximation for the SRO parameters. Within this approximation one can calculate the Fourier transform $\alpha_{\mathbf{k}}^{ij}$ of the SRO parameters using Eq. (123) and then the parameters $\alpha_{\mathbf{R}}^{ij}$

themselves by integration over the Brillouin zone [see Eq. (117)]. In Eq. (123) the matrix $\beta_{\mathbf{k}}^{-1}$ (ring) is inverse to $\beta_{\mathbf{k}}^{\text{ring}}$ defined in Eq. (87), where the quantities μ_i are determined from Eq. (39).

The ring approximation is a generalization of the corresponding approximation derived in Ref. 17 [see Eqs. (7.6) and (7.7) there] to the case of the lattice gas with a complex crystal lattice and with a LRO. Besides, the chemical potential fluctuations were taken into account in Eq. (123) and the correct equations for determination of the chemical potentials were used (see discussion in Ref. 18). The particular case of the ring approximation (123) is the spherical model approximation (119) corresponding to the neglect of all terms except for $A_{\mathbf{k}}^{ij}$ in the expression (87) for $\beta_{\mathbf{k}}^{ij}$.

Within the MF approximation, by use of the thermodynamic fluctuation method, we obtain

$$\alpha_{\mathbf{k}}^{ij} = \|\beta_{\mathbf{k}}^{-1}(\text{MF})\|_{ij}, \quad (124)$$

where $\|\beta_{\mathbf{k}}^{-1}(\text{MF})\|_{ij}$ is the ij element of the matrix that is inverse to $\beta_{\mathbf{k}}^{\text{MF}}$ with the elements $\beta_{i,j,\mathbf{k}}^{\text{MF}}$ defined in Eq. (109).

$$\alpha_{\mathbf{k}}^{ij} = \begin{cases} 1 - N^{-1} \sum_{\mathbf{q}} \|\beta_{\mathbf{q}}^{-1}(\text{ring})\|_{ii} + \|\beta_{\mathbf{k}}^{-1}(\text{ring})\|_{ii} & \text{if } i=j \\ \|\beta_{\mathbf{k}}^{-1}(\text{ring})\|_{ij} & \text{otherwise.} \end{cases} \quad (125)$$

instead of Eq. (123). The normalization results in more complicated expressions and calculations. However, such a normalization is unimportant for physical results because it has no effect on the SRO parameters for nonzero coordination shells. In the reciprocal space normalization also results in only uniform shift of $\alpha_{\mathbf{k}}^{ij}$ without any effect on its shape. By the numerical calculations we found that the violation of the constraint (116) is remarkable only within the critical regions of the phase diagram, where the ring approximation gives a large error itself. Besides, the normalization violates the fluctuation-dissipation theorem.³⁶ The normalization by a multiplier suggested in Ref. 51 is less justified and is not feasible if the number of sublattices is more than one. Thus, in the present paper we suggest not to use any normalization at all, although of course one can use the expressions such as Eq. (125). The value of violation of the constraint (116) can serve as a numerical criteria for applicability of an approximation (see also Sec. 4.2.4 in Ref. 14).

D. Case of the disordered lattice gas with a Bravais crystal lattice

In such a particular case it is not necessary to introduce the sublattice index i and instead of Eqs. (119), (123), and (124) we have

$$\alpha_{\mathbf{k}} = \left\{ 1 + \frac{c(1-c)}{k_{\text{B}}T} [\mu + \tilde{\Phi}_{\mathbf{k}}^{(2)}] \right\}^{-1}, \quad (126)$$

We shall call the obtained expression (124) as the MF approximation for the SRO parameters.

In case of the disordered state with a Bravais crystal lattice, Eq. (124) transforms into Eq. (2.13) in Ref. 20. In case of the disordered state with a complex crystal lattice and only pair atomic interactions, Eq. (124) transforms into Eq. (II2.16) in Ref. 50 (neglecting there the normalization by multiplier). In case of the disordered state with a Bravais crystal lattice and only pair atomic interactions, Eq. (124) transforms into the Krivoglaz approximation [Eq. (34.50) in Ref. 9].

C. Normalization

The obtained expressions for SRO within the ring (123) and MF (124) approximations [in contrast to the spherical model one (119)] do *not* satisfy the constraint (116). Previously, the normalization by summands was suggested in Refs. 2,15 in order to improve the situation. For example, in such a way we would get

$$\alpha_{\mathbf{k}} = [\beta_{\mathbf{k}}^{\text{ring}}]^{-1}, \quad (127)$$

and

$$\alpha_{\mathbf{k}} = [\beta_{\mathbf{k}}^{\text{MF}}]^{-1} \quad (128)$$

within the spherical model, ring, and MF approximations for the SRO, respectively, where

$$\alpha_{\mathbf{k}} = \sum_{\mathbf{R}} \alpha_{\mathbf{R}} \exp(-i\mathbf{k}\mathbf{R}), \quad \alpha_{\mathbf{R}_1 - \mathbf{R}_2} = \frac{\langle\langle C_{\mathbf{R}_1} C_{\mathbf{R}_2} \rangle\rangle - c^2}{c(1-c)} \quad (129)$$

($\alpha_{\mathbf{R}}$ are the usual Warren-Cowley parameters⁴⁷), $\beta_{\mathbf{k}}^{\text{ring}}$ is defined in Eq. (102),

$$\beta_{\mathbf{k}}^{\text{MF}} = 1 + \frac{c(1-c)}{k_{\text{B}}T} \tilde{\Phi}_{\mathbf{k}}^{(2)}, \quad (130)$$

$\tilde{\Phi}_{\mathbf{k}}^{(2)}$ is defined in Eq. (46) at $n=2$. The quantity μ in Eqs. (126) and (127) is determined from the same equation [see Eq. (39)]

$$N^{-1} \sum_{\mathbf{k}} \left\{ 1 + \frac{c(1-c)}{k_{\text{B}}T} [\mu + \tilde{\Phi}_{\mathbf{k}}^{(2)}] \right\}^{-1} = 1. \quad (131)$$

The expressions (126) and (128) have been obtained in Refs. 17,20 and are presented here for completeness. The expression (127) is the generalization of that one obtained in

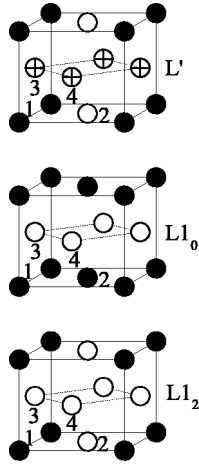


FIG. 2. The unit cells of $L1_2$, $L1_0$, and $L'(P4/mmm)$ superstructures (e.g., Ref. 54). The atoms within the unit cells are enumerated in all cases. The sites with different values of P_i are marked differently.

Ref. 18 to the case of presence of the nonpair atomic interactions. Neglecting the nonpair atomic interactions, one can also find similarities between $\beta_{\mathbf{k}}^{\text{ring}}$ at $\mu=0$ and the expression for the spin correlation function obtained in Ref. 52 [see Eqs. (20) and (22) there or Sec. 16.3 in Ref. 53] within the Ising model by use the inverse radius of spin interactions as a small parameter of the diagram expansion.

X. PHASE DIAGRAM CALCULATION

At given interatomic mixing potentials, using Eqs. (38) and (39), one can calculate the free energy of the lattice gas with any complex crystal lattice and any type of LRO. To achieve this aim it is necessary to know the unit cell of the superstructure and the expression of the probabilities P_i through the LRO parameters. Then, the minimization of the free energy functional with respect to the LRO parameters has to be made by a direct numerical minimization and/or by solving of the corresponding equations of state (66).

For example, in the cases of $L1_2$, $L1_0$, and $L'(P4/mmm)$ superstructures of the two-component lattice gas (studied below in Sec. XIII), all the unit cells can be chosen to be composed of four sites of the fcc crystal lattice (see Fig. 2) with

$$\left. \begin{aligned} P_1 &= c + 3/4\eta \\ P_2 &= P_3 = P_4 = c - 1/4\eta \end{aligned} \right\} [L1_2], \quad (132)$$

$$\left. \begin{aligned} P_1 &= P_2 = c + 1/2\eta \\ P_3 &= P_4 = c - 1/2\eta \end{aligned} \right\} [L1_0], \quad (133)$$

$$\left. \begin{aligned} P_1 &= c + 1/4\eta_1 + 1/2\eta_2 \\ P_2 &= c + 1/4\eta_1 - 1/2\eta_2 \\ P_3 &= P_4 = c - 1/4\eta_1 \end{aligned} \right\} [L'(P4/mmm)], \quad (134)$$

where c is the concentration and η is the LRO parameter(s). Being completely ordered, $L1_2$, $L1_0$, and $L'(P4/mmm)$

structures have the stoichiometric concentrations 0.25, 0.50, and 0.25, respectively, and all LRO parameters being equal to unity.

By a comparison of the free energies of all structures and their mixtures (by a common tangents method) supposed to be competitive at the considered external conditions, one can calculate the complete phase diagram of the system in question.⁵⁵ In order to find the set of structures to be put into competition one can use the corresponding experimental data. For the case of poor or unreliable experimental data we can suggest the following procedure.⁵⁵

Being in a region of the phase diagram where some structure is thermodynamically stable, we calculate the lower critical temperature T_c of the absolute instability of this structure as well as the instability wave vectors $\mathbf{k}_0^{(l)}$ ($l=1, 2, \dots$) by using Eq. (97). Then we introduce the concentration waves²⁵⁻²⁷ corresponding to $\mathbf{k}_0^{(l)}$,

$$P_{i,\mathbf{R}} = c + \sum_l \zeta_{il} \exp[i\mathbf{k}_0^{(l)}\mathbf{R}] \leftrightarrow P'_i, \quad (135)$$

(c is the concentration of A-type atom). According to the space periodicity of $P_{i,\mathbf{R}}$ we choose the *new* unit cell. The probability distribution P'_i , within that new cell is determined by the minimization of the corresponding free energy functional either with respect to P'_i , (with the constraint $\sum_{i'=1}^{v'} P'_{i'} = v'c$) or with respect to the coefficients ζ_{il} containing the information about the *type* of a new structure as well as about the values of the corresponding LRO parameters. The first way is more general (because we also take into account some $\mathbf{k} \notin \{\mathbf{k}_0^{(l)}\}$) but more time consuming because the number of P'_i is usually much larger than that of ζ_{il} .

Being in the region of the phase diagram where the new structure found at the previous step is thermodynamically stable, we repeat the above procedure and so on. By such way, beginning from the disordered state at high temperatures and then decreasing the temperature, we can find all competitive structures in all temperature-concentration regions and then calculate the complete phase diagram.

The described procedure is similar to the one proposed by Bugaev and Ryzhkov²² (see also Sec. 7 in Ref. 21). However, we use the ring approximation instead of the MF one. Besides, we suggest to minimize the free energy (obtained within the ring approximation) with respect to the coefficients ζ_{il} . In Ref. 22, according to the method of static concentration waves (SCW),²⁵⁻²⁷ the coefficients ζ_{il} are presented as multiplication of the LRO parameters and structural coefficients. Thereby, one LRO parameter is put into correspondence to one irreducible representation of the corresponding space group. The structural coefficients are to be found from the pure symmetry consideration whereas the LRO parameters are determined by a minimization of the free energy (by the use of the corresponding equations of state).

However, if we put only one LRO parameter into correspondence to one irreducible representation of the corresponding space group,⁵⁶ we cannot describe some possible

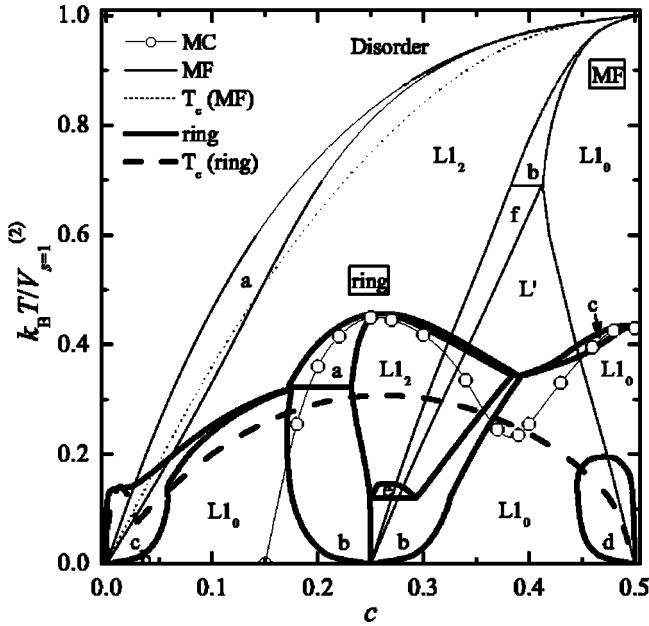


FIG. 3. Phase diagrams calculated within the ring (ring) and mean-field (MF) approximations in the case of the two-component lattice gas with fcc crystal lattice (in the disordered state) and with $V_{s=1}^{(2)} > 0$. $V_s^{(n)}$ is the value of the n th order mixing potential for the s th coordination shell (see Sec. 4 in Ref. 20) of the fcc crystal lattice. All the other mixing potentials except the denoted one are equal to zero. MC is the designation of the order-disorder phase transformation temperatures corresponding to the abrupt change in the temperature dependence of the SRO parameters simulated by the Monte Carlo method according to Sec. 2 in Ref. 15 (see also Refs. 60–62). T_c is the critical temperature of the absolute instability of the disordered state. The description of the structures is presented in Fig. 2 and in Sec. X. The regions corresponding to a mixture of two structures are denoted as (a) disorder+ $L1_2$, (b) $L1_0+L1_2$, (c) disorder+ $L1_0$, (d) $L1_0+L1_0$, (e) $L1_2+L1_2$, and (f) $L1_2+L'$.

structures corresponding to the wave vectors appropriate to those representations. For example, in the case of fcc Bravais crystal lattice (when one representation corresponds to one star of the wave vectors), the method of SCW gives only $L1_0$ and $L1_2$ structures corresponding to $X(0,0,1)$ (and only X) star of the wave vectors.^{25–27,57} (Here and below, we present the Cartesian coordinates of points in the reciprocal space in units of $2\pi/a$, where a is the lattice parameter.) Thus, within the method of SCW it is impossible to describe L' ($P4/mmm$) structure, which also corresponds to $X(0,0,1)$ (and only X) star and can be stable in wide temperature-concentration intervals of the phase diagrams (see Refs. 54,58, Sec. 4.4.1, in Ref. 14 and Fig. 3).

The above-proposed minimization of the free energy with respect to the coefficients ζ_{il} (which are put into correspondence to each wave vector in expansion (135) rather than to each irreducible representation) allows to avoid such shortcoming as well as allows to unify the determination of both the type of the structure and the values of the LRO parameters.

The above-described procedure (just like that of Bugaev and Ryzhkov²²) unifies the Fourier analysis^{25–27} with taking

into account the space (both direct and reciprocal) symmetry differences of superstructures within the sublattice formalism. Despite the use of the sublattice formalism, *a priori* assumptions on the superstructures to be appeared at disorder-order and order-order phase transitions are not necessary within our procedure (in contrast to the method developed in Refs. 9,59). It is important that the instability wave vectors corresponding to the high-symmetry (stationary) points of the reciprocal space of a given superstructure may not correspond to the high-symmetry points of the corresponding parent disordered structure.²² Within the ring approximation (in contrast to the MF one^{25–27}), even in the case of the pair atomic interactions, disordered structure, and Bravais crystal lattice, the instability wave vectors are not generally determined by the minima of the Fourier transform of the pair mixing potential in the reciprocal space (see examples below in Sec. XIII and also the discussion at the end of Sec. 11 in Ref. 5).

XI. MULTICOMPONENT LATTICE GAS

The above-obtained results can be directly applied not only in the case of a *two*-component lattice gas $A-B$ but also in the cases when for each i th sublattice there are only *two* types of atoms A_i and B_i for which the i th sublattice is allowed to be occupied. It is not generally the case of a two-component lattice gas because those two types of atoms may be different for different sublattices. For example, it is the case of a three-component substitutional-interstitial $A-B-X$ lattice gas in which all the substitutional sites are occupied by A - and B -type atoms and all the interstitial sites are occupied by X -type atoms and vacancies.

In such more general cases, all the obtained expressions are just the same. Only we have to change A to A_i in definition 3 of the configurational variable $C_{i,R}$ (all types B_i are excluded from the configurational description—see Sec. 2 in Ref. 21). Accordingly, P_i will be the probability of finding an A_i -type atom at a site belonging to the i th sublattice. Of course, in the case of the disordered state with a Bravais crystal lattice, we may consider only a two-component lattice gas.

In general case of a multicomponent lattice gas in which at least one sublattice is allowed to be occupied by more than two types of atoms, the above-obtained formulas are not valid and must be generalized.

XII. HEAT CAPACITY IN THE DISORDERED STATE

In a general case of the disordered state, we put temperature independent $P_i = c_i$ ($i = 1, 2, \dots, \nu$), where c_i is the concentration of A_i -type atoms (see Sec. XI). [In the particular case of a two-component lattice gas, $c_i = c$ ($i = 1, 2, \dots, \nu$), where c is the concentration A -type atoms.] From Eq. (41), within the ring approximation, assuming that the mixing potentials are independent from the temperature, we obtain for the configurational heat capacity c_V

$$c_V = \frac{\partial \varepsilon_{\text{ring}}}{\partial T} = - \sum_i \frac{c_i(1-c_i)}{2} \frac{\partial \mu_i}{\partial T}. \quad (136)$$

TABLE I. The values of the order-disorder phase transformation temperatures T_0 at $c=0.25, 0.5$ obtained by MC simulation, by series expansion (SE) (from Table III in Ref. 5), by cluster-variation method in tetrahedron-octahedron approximation (CVM) (Ref. 58), within the MF and ring approximations in the case (see Fig. 3) of the two-component lattice gas with fcc crystal lattice (in the disordered state) and with $V_{s=1}^{(2)} > 0$. $V_s^{(n)}$ is the value of the n th-order mixing potential for the s th coordination shell (see Sec. 4 in Ref. 20) of the fcc crystal lattice. All the other mixing potentials except the denoted one are equal to zero. All the temperatures are in units of $k_B/V_{s=1}^{(2)}$.

T_0	$c=0.50$	$c=0.25$
MC	0.43	0.449
SE	0.4365	
Ring	0.4363	0.4566
CVM	0.4525	0.465
MF	1	0.827

From Eq. (39), one can get that

$$\frac{c_i(1-c_i)}{k_B} \frac{\partial \mu_i}{\partial T} = \sum_j \|I_0^{-1}\|_{ij} - 1, \quad (137)$$

where $\|I_k^{-1}\|$ is the matrix inverse to that one whose elements I_k^{ij} are defined in Eq. (89) (with $P_i=c_i$). Substituting Eq. (137) into Eq. (136), we have

$$c_V = \frac{k_B}{2} \left\{ \nu - \sum_{i,j} \|I_0^{-1}\|_{ij} \right\}. \quad (138)$$

In the particular case of a two-component lattice gas with a Bravais crystal lattice

$$c_V = \frac{k_B}{2} \left(1 - \frac{1}{I} \right), \quad (139)$$

where

$$I = \frac{1}{N} \sum_{\mathbf{k}} \left\{ 1 + \frac{c(1-c)}{k_B T} [\mu + \Phi_{\mathbf{k}}^{(2)}] \right\}^{-2}. \quad (140)$$

Note that within the MF approximation the configurational heat capacity of the disordered state is equal to zero in contrast to the ring approximation (if $T \neq \infty$). It is just the interatomic correlations that contribute to the configurational heat capacity of the disordered state within the ring approximation in contrast to the MF one.

XIII. NUMERICAL CALCULATIONS

A. Phase diagrams

As an example of the phase diagram calculation and with the aim to study the numerical accuracy of the ring approximation, we considered four model cases presented in Table I and Figs. 3–6. All the cases are appropriate to the two-component lattice gas that has fcc crystal lattice in the disordered state. The pair and triplet atomic interactions of the nearest and next-nearest neighbors are taken into account in

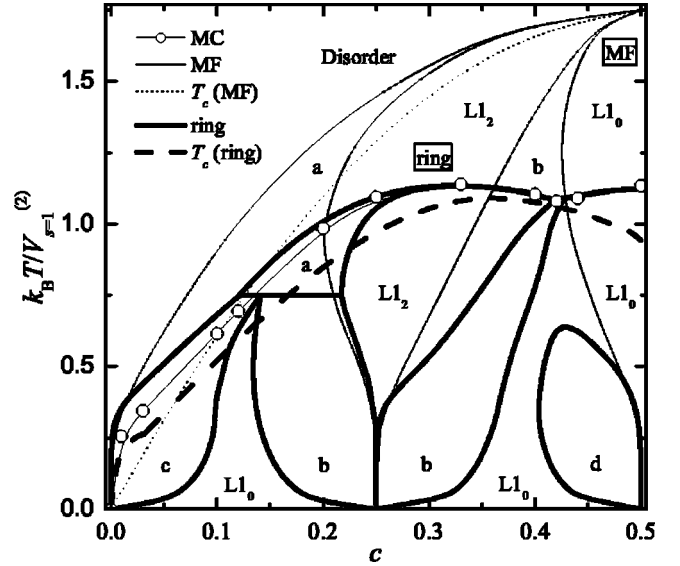


FIG. 4. The same as in Fig. 3, but in the case of $V_{s=1}^{(2)} > 0$, $V_{s=2}^{(2)} = -0.5V_{s=1}^{(2)}$.

different combinations for different cases (see captions to figures). The interatomic mixing potentials are assumed to be structure independent (see Appendix D) and to have the symmetry of the *disordered* state. The corresponding phase diagrams were calculated within the ring and MF approximations following the procedure suggested in Sec. X. (Our MF approximation results presented in Figs. 3 and 4 are adequate to those in Ref. 54; see also Sec. 5.2.4 in Ref. 14.) The order-disorder (Figs. 3–5) and decomposition (Fig. 6) phase transformation temperatures were also calculated by the MC simulation. Note that in the cases corresponding to Figs. 3 and 4, the consideration of the concentrations greater than

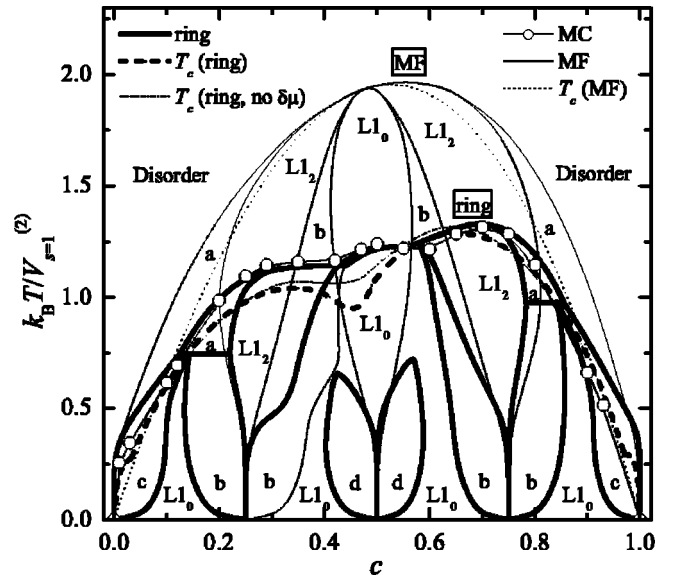


FIG. 5. The same as in Fig. 3, but in the case of $V_{s=1}^{(2)} > 0$, $V_{s=2}^{(2)} = -0.5V_{s=1}^{(2)}$, $V_{s=3}^{(2)} = 0.1V_{s=1}^{(2)}$. “no $\delta\mu$ ” means that T_c was calculated not taking into account the chemical potential fluctuations within the ring approximation.

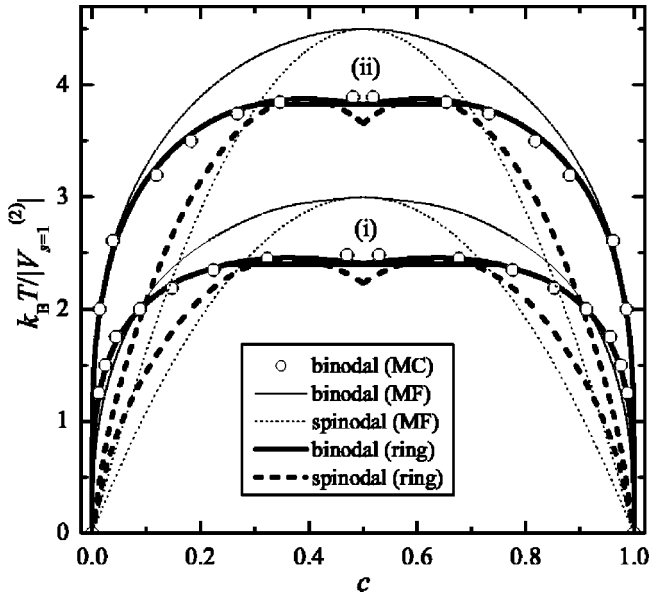


FIG. 6. The same as in Fig. 3, but in the cases of (i) $V_{s=1}^{(2)} < 0$, $V_{s=2}^{(2)} = 0$, (ii) $V_{s=1}^{(2)} < 0$, $V_{s=2}^{(2)} = V_{s=1}^{(2)}$. The MC simulation data were taken from Ref. 63. Solid and dashed lines correspond, respectively, to the binodals (miscibility gaps) and spinodals of the decompositions into two disordered phases of different concentrations.

the equiatomic one is not required due to the symmetry of the phase diagram with respect to equiatomic concentration in the case of lattice gas with concentration-independent atomic interactions of less than or equal to the second order.²⁰

Accepting the results of the MC simulation as a standard, on the basis of the data presented in Table I and Figs. 3–6, one may conclude the following.

In all the considered cases the ring approximation yields the adequate results in wide temperature-concentration intervals. The phase transformation temperatures are predicted much more accurately within the ring approximation than in the MF one in all the considered cases. At low temperatures the numerical accuracy of the ring approximation data is lower in the cases of ordering. Namely, from Figs. 3–5 it follows that at low temperatures the ring approximation predicts the stability of $L1_0$ structure in wide concentration intervals. $L1_0$ occurs to be the unique ground-state structure for all concentrations (but $c = 0; 0.25; 0.75; 1$) within the ring approximation in all three considered cases. Such results are in contradiction with those of the MF approximation (Figs. 3–5 and Ref. 54), MC simulation,^{60,61} and cluster-variation method (CVM),^{58,64} where at low temperatures (including $T = 0$) we have $L1_2$ and L' structures⁶⁵ or the mixtures of pure component, $L1_0$ and $L1_2$ structures to be stable in the corresponding cases.

Thus, one can conclude that the ring approximation gives inadequate results at low temperatures probably unreasonably decreasing the free energy of $L1_0$ structure. Such wrong predictions within the ring approximation can be explained by two reasons. First, as noted in Sec. VI, the contribution of the neglected reducible diagrams in the cumulant expansion

can be considerable at low temperatures. Second, the ring approximation can be sensitive to the frustration effects, which are strong at low temperatures in case of short-range atomic interactions.^{14,58,66} Fortunately, there is a strong tendency of decreasing the regions of unreasonable stability of $L1_0$ structure in phase diagram calculated within the ring approximation when the atomic interactions of the next-nearest neighbors are taken into account (compare Figs. 3 and 4). So, one can expect that in case of actual systems with long-range atomic interactions the ring approximation will be applicable at sufficiently low temperatures. If the frustration effects are important for a low numerical accuracy of the ring approximation at low temperatures, one can expect also the increase of such an accuracy under taking into account the structural dependence of atomic interactions, which diminishes the frustration effects. Note that the same problem of adequate description of the low-temperature regions was also revealed within the MF and CVM in the two-dimensional case (e.g., Ref. 67).

The discrepancy between the MC and ring approximation data occurs to be considerable only in case of pair nearest-neighbor atomic interactions (see Fig. 3) at $c < 0.18$ ($c > 0.82$). However, in this case one can *a priori* expect the problem of adequate description within the ring approximation in which the inverse value of the effective number z of atoms interacting with one fixed atom is chosen as a small parameter in the corresponding perturbation theory. At sufficiently low (or high) concentrations, in all temperature intervals the free energy is lowest for random distribution of non-interacting atoms, when each atom has no nearest neighbors. So there is no order-disorder phase transformation at such concentrations down to and including $T = 0$ (see MC curve in Fig. 3). But in such a case $z = 0$ and the ring approximation must be inapplicable.

The numerical accuracy of the ring approximation data is low in the case of pair nearest-neighbor atomic interactions (see Fig. 3) in the vicinity of the triple point near $c = 0.40$ ($c = 0.60$). However, the problem of adequate description of the vicinity of the triple point is well known and is attributed to the “frustration” character of the corresponding model case due to the strongly degenerate ground state.^{14,58,66} One encounters this problem within both the MC⁶² and CVM^{58,68} (see also Ref. 8 and Sec. 5.1.5 in Ref. 14). Taking into account the next-neighbor interactions allows to resolve the problem diminishing such a degeneracy (compare Figs. 3 and 4).

In the cases of decomposition into two disordered phases of different concentrations (Fig. 6), the quantitative correspondence between MC and ring approximation data is excellent and much better than that between MC and MF. Nevertheless, there are qualitative discrepancies between the results of the MC simulation and MF approximation on one hand and of the ring approximation on other hand. Namely, in contrast to the MC simulation⁶³ and MF approximation data, within the ring approximation we have (a) the decomposition into two disordered phases of concentrations c_1 and c_2 with $c_1 + c_2 \neq 1$ in very small temperature intervals at the top of the phase diagrams and (b) the phase transformation of the *first* order at $c = 0.5$.⁶⁹ According to our unpublished

calculations within CVM (see also Refs. 4,5,70–72), such behavior of the ring approximation is also in contradiction with CVM. The same problem of adequate description of the order of the phase transformation was also revealed within the approximations that are similar to the ring one^{12,24,33,36,42,73} and even within CVM (in the two-dimensional case, see Sec. 10 in Ref. 5). According to our above discussion in Sec. VI, such inadequacy of the ring approximation can be caused by the proximity of the binodal (miscibility gap) and spinodal in the corresponding T - c region of the phase diagram. (By the binodal or miscibility gap we mean the curve corresponding to the concentrations of two coexisting phases at decomposition; by spinodal we mean the critical temperature of absolute instability of homogeneities disordered state, see e.g., Ref. 4.)

It should be emphasized that all the considered cases corresponding to atomic interactions of only nearest and next-nearest neighbors are obviously most unfavorable as for a high numerical accuracy of the ring approximation in which z^{-1} is chosen as a small parameter in the corresponding perturbation theory. Additional problems are caused also by frustration effects, which are strong in the considered cases. Our choice of the considered cases was dictated by an easy realization of the corresponding MC simulation, by presence of the corresponding data obtained within other approximations and by desire to study the main *tendencies* of the numerical accuracy of the ring approximation. Besides, the consideration of the fcc crystal lattice is also unfavorable in comparison with that of the bcc one.⁴ Surprisingly, even in such unfavorable cases the ring approximation demonstrates its adequacy in wide T - c regions. The high numerical accuracy of this approximation even in the cases of the short-range atomic interactions as well as the essential increase of the accuracy when the atomic interactions for the next-nearest neighbors are taken into account clearly demonstrate the quick convergence of the cumulant expansion under such a choice of a small parameter as in the ring approximation.

In Figs. 3–6 we also presented the critical temperature T_c of the absolute instability of the disordered state calculated within the ring (106) and MF (113) approximations. In the case of decomposition (see Fig. 6), within both the MF and ring approximations the instability wave vector $\mathbf{k}_0=(0,0,0)$ (Γ point) in all concentration region. In the case of ordering (see Figs. 3–5), within the MF approximation the instability wave vector $\mathbf{k}_0=(1,0,0)$ (X point) in *all* concentration region. Within the ring approximation $\mathbf{k}_0=(1,0,0)$ (X point) in a wide concentration region. However, at very small and big concentrations, where T_c curve demonstrates nonmonotonic change, $\mathbf{k}_0=(0,0,0)$ (Γ point). So, in such a particular (but important) case of the disordered state, we demonstrated the possibility to describe the concentrational dependence of the instability wave vector \mathbf{k}_0 within the ring approximation in contrast to the MF one.

In Fig. 5 we also presented T_c calculated not taking into account the chemical potential fluctuations within the ring approximation [i.e., at $\delta\mu_{i,\mathbf{R}}\equiv 0$ in Eq. (81)]. As it follows from Fig. 5, the neglect of the chemical-potential fluctuations can be noticeable and can erroneously make the value of

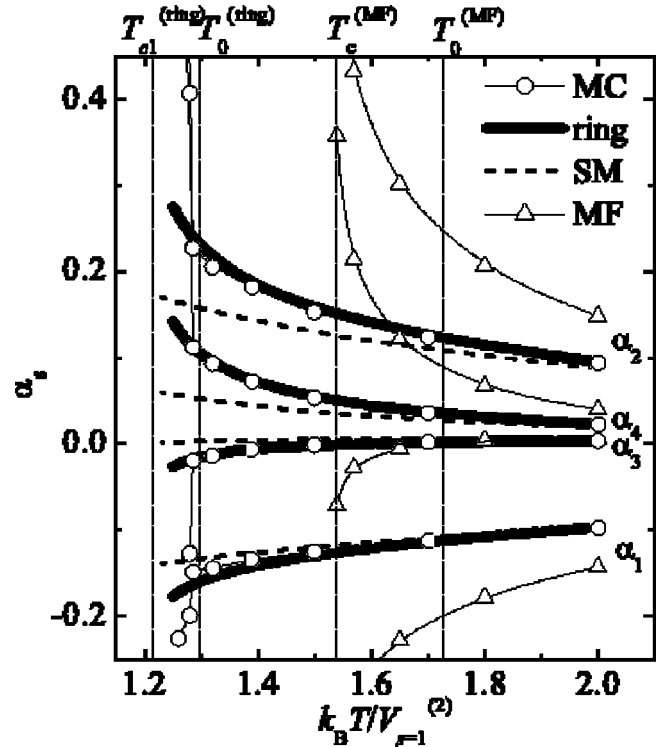


FIG. 7. Temperature evolution of the SRO parameters $\alpha_i \equiv \alpha_{\mathbf{R}_i}$ for the first four coordination shells ($i=1,2,\dots,4$) of the fcc disordered two-component lattice gas calculated in the framework of the spherical model (SM) (126), ring (Ring) (127), and mean field (MF) (128) approximations as well as obtained by the Monte Carlo simulation (MC) at $c=0.75$, $V_{s=1}^{(2)} > 0$, $V_{s=2}^{(2)} = -0.5V_{s=1}^{(2)}$, $V_{s=1}^{(3)} = 0.1V_{s=1}^{(2)}$. \mathbf{R}_s is the radius vector of a site belonging to the s th coordination shell. The MC simulation was performed in accordance with the procedure described in Sec. 2 of Ref. 15. T_{c1} and T_0 are the temperatures of the absolute instability of the disordered state and of the order-disorder phase transformation, respectively, calculated within the ring and MF approximations. The point of the abrupt change of the MC curves corresponds to the order-disorder phase transformation within the Monte Carlo simulation.

such critical temperature be even more than the temperature of the order-disorder phase transformation.

B. Short-range order

As an example of the SRO calculation, we considered the fcc disordered two-component lattice gas with concentration $c=0.75$ and with the same atomic interactions as in the case presented in Fig. 5. The corresponding results of calculations are shown in Fig. 7. Note that the SRO at temperatures lower than the temperature of the order-disorder phase transformation corresponds to the metastable disordered state.

Accepting the results of the MC simulation as a standard, from Fig. 7 it follows that the ring approximation yields the results of high numerical accuracy in wide temperature interval down to the temperature of the order-disorder phase transformation. The numerical accuracy of the ring approximation is higher than that of the spherical model, especially for the coordination shells with big radius. The numerical accuracies of both the ring and spherical model approxima-

tions is much higher than that of the MF one. It should be noted also that within the ring approximation (in contrast to the MF and spherical model ones) it is possible to describe the important phenomenon of the temperature dependence of the positions of the SRO peaks in the reciprocal space for lattice gas even with constant atomic interactions. We do not study this phenomenon in the present paper because much attention was given to it earlier.^{46,74–76}

XIV. CONCLUSIONS

In the present paper the general method was elaborated for the statistical-thermodynamic description within the ring approximation of the lattice gas with a complex crystal lattice and with nonpair atomic interactions of any order and effective radii of action. By this method one can calculate the complete phase diagram of the lattice gas (Sec. X) as well as the atomic correlation function (in real and reciprocal space) in both disordered and LRO states of it (Sec. IX).

The elaborate method is general and analytically simple. The corresponding analytical expressions do not change their form at an increase of the effective radius of atomic interactions and are valid in case of any superstructure. The number of the variational parameters for minimization of the free energy is considerably fewer than that one within the cluster variation method (CVM) (see Sec. 4 in Ref. 19) resulting in the considerable reduction of the time for the corresponding computer calculations. It is important that, within the ring approximation, these numbers of the variational parameters are determined only by the type of the structure and are independent from the value of the effective radius of atomic interactions in contrast to CVM. Of course, due to the analytical nature of the ring approximation, the time for calculations within it is much less than that of the MC simulation. Within the ring approximation, the difference of the space symmetries of the interatomic potentials for different structures²¹ can easily be taken into account.

The ring approximation offers the principal advantage over MC and CVM for a description of actual alloys in which the elastic distortions induce extremely long-range atomic interactions. It is because the Fourier transform of the strain-induced interatomic potential of such alloys has a nonanalyticity, which cannot be described in terms of the values of the potential for any great but finite number of coordination shells (e.g., Sec. 7a in Ref. 4). However, within the ring approximation (in contrast to MC and CVM) it is not necessary to approximate the interatomic potentials by its values for a finite number of coordination shells because the potentials appear in the corresponding expressions only through their Fourier transforms.

The applicability of the ring approximation is discussed on the basis of theoretical consideration (Sec. VI) as well as by a comparison of the numerical results with the corresponding MC simulation (Sec. XIII). The high numerical accuracy of the ring approximation was demonstrated in wide temperature-concentration intervals in the case of short-ranged atomic interactions. The tendency of increase of the numerical accuracy of the ring approximation with increase of the effective radius of atomic interactions (and the dimen-

sionality of the crystal lattice³⁶) was shown in accordance with the Brout z^{-1} classification.

The ring approximation demonstrates the comparatively low numerical accuracy at sufficiently low temperatures in case of nonstoichiometric compositions and short-ranged atomic interactions. Such wrong predictions within the ring approximation can be explained by two reasons. First, the contribution of the neglected reducible diagrams in the cumulant expansion can be considerable at low temperatures. Second, the ring approximation can be sensitive to the frustration effects, which are strong at low temperatures in case of short-range atomic interactions.^{14,58,66} Fortunately, there is a strong tendency of decrease the low-temperature regions of low accuracy of the ring approximation with increase of the radius of atomic interactions. So one can expect that in case of actual systems with long-range atomic interactions the ring approximation will be applicable at sufficiently low temperatures. If the frustration effects are important for a low numerical accuracy of the ring approximation at low temperatures, one can also expect the increase of such an accuracy taking into account the structural dependence of atomic interactions, which diminishes the frustration effects.

It should be added that, from the practical point of view, the most interesting part of the phase diagram is the order-disorder phase transformation rather than the low-temperature regions. Besides, at low temperatures the relaxation can be so slow that the thermodynamically stable states cannot be reached in reasonable time. (That is the reason why the low-temperature calculations are problematic within MC and CVM, see e.g., Ref. 8 and Sec. 5.1.5 in Ref. 14.) Because of the Nernst theorem, when the atomic interactions are *not* frustrated, at $T \rightarrow 0$ we have a mixture of almost completely ordered structures whose concentrations are close to the corresponding stoichiometric ones (e.g., Sec. 12 in Ref. 9 and Ref. 49). Thus, in the low-temperature region we can use the theory of almost completely ordered structures or even the MF approximation, which is applicable at low temperatures for description of structures with almost stoichiometric concentrations (Sec. 19 in Ref. 9). Besides, we found that within the ring approximation in case of the stoichiometric compositions, there is no problem of low numerical accuracy at low temperatures.

In the case of short-ranged atomic interactions, the ring approximation gives comparatively big error for evaluation of the temperatures of the phase transformations of the second or close to second orders. However, in real lattice systems such phase transformations are very rarely encountered. Account of structural dependence and/or long-range character of atomic interactions result in change of order of phase transformations from the second to first (e.g., Sec. 4.4 in Ref. 45). Besides, actually such MF-like theories as the ring approximation and CVM are not intended to be used for a description of the critical phenomena but rather for description of phase diagrams, correlation effects, nonequilibrium processes, etc. outside the critical regions, which nevertheless is of great interest from practical point of view (e.g., Chap. 5 in Ref. 4, Secs. 4.1 and 4.5.6 in Ref. 14). For a description of the critical phenomena and universal characteristics of phase transitions, we have to use the special

methods (e.g., series expansions and renormalization-group theory).

Thus, the ring approximation being an example of the wave (or reciprocal-space) methods⁴ can be recommended for the statistical-thermodynamic description of the lattice-gas model with long-range atomic interactions along with MC and CVM,³⁵ which are the examples of the cluster (or direct-space) methods.⁴ The ring approximation as well as CVM are the examples of closed form approximations. The advantages of such approximations over the series expansion methods are discussed in Ref. 77. Being much simpler than MC and CVM, the ring approximation can be particularly useful at consideration of complex situations like vicinal surfaces.²⁴ Being a single-site theory, the ring approximation can be easily implemented within first-principles electronic methods.

At calculation of phase diagram within the ring approximation it is also possible to include into consideration the metastable structures (which may be important at low temperatures due to the slow relaxation), the long-period structures and the structures with different parent crystal lattices (being actual in case of, for example, Cu-Zn, Pt-V, and Cu-Pt alloy systems). Within MC and CVM the consideration of such structures is hardly feasible in contrast to the ring approximation.

The detailed numerical study of the ring approximation performed in the present paper can help to understand the features of similar approximations as well (see Sec. V). The ring approximation has been already successfully used for study of Ni-V,^{46,74} Ni-H,⁷⁸ and Cu-Pd⁷⁶ alloys. It can be also applied in the case of multicomponent lattice gas (see Sec. XI). The approach advanced in the present work may be extended to the case of the Ising model.³⁶ 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 (see also Ref. 36). 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.¹²

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APPENDIX A

Performing the Fourier transformation in Eq. (24) and introducing the Hermitian matrix F with the elements

$$F_{i_1, i_2} = - \frac{\sqrt{P_{i_1}(1-P_{i_1})} [\mu_{i_1} \delta_{i_1, i_2} + \tilde{\Phi}_{i_1, \mathbf{k}; i_2}^{(2)}] \sqrt{P_{i_2}(1-P_{i_2})}}{k_B T}, \quad (\text{A1})$$

one can obtain

$$\Delta f_1 = - \frac{k_B T}{2N} \sum_{\mathbf{k}} \sum_{n=1}^{\infty} \frac{1}{n} \text{Tr} F^n. \quad (\text{A2})$$

Let us introduce also the diagonal matrix Ψ with the elements

$$\Psi_{ij} = \psi_i \delta_{ij} \quad (\text{A3})$$

(δ is the Kronecker delta) that is the unitary transformation of the matrix F ,

$$F = U^{-1} \Psi U. \quad (\text{A4})$$

Note that ψ_i are the eigenvalues of the matrix F and the unitary matrix U can be built through the eigenvectors of the matrix F .

Because

$$\text{Tr} F^n = \text{Tr} \Psi^n = \sum_i \psi_i^n, \quad (\text{A5})$$

the expression (A2) can be rewritten as

$$\Delta f_1 = - \frac{k_B T}{2N} \sum_{\mathbf{k}} \sum_i \sum_{n=1}^{\infty} \frac{1}{n} \psi_i^n = \frac{k_B T}{2N} \sum_{\mathbf{k}} \ln \prod_i (1 - \psi_i). \quad (\text{A6})$$

Taking into account that

$$\begin{aligned} \det(\Delta - F) &= \det[U(\Delta - F)U^{-1}] \\ &= \det(\Delta - \Psi) = \prod_i (1 - \psi_i), \end{aligned} \quad (\text{A7})$$

where Δ is the unity matrix with elements δ_{ij} , from Eq. (A6) we finally have

$$\Delta f_1 = \frac{k_B T}{2N} \sum_{\mathbf{k}} \ln \det(\Delta - F). \quad (\text{A8})$$

The expression (A8) is identical to Eq. (32) because [see Eqs. (33) and (A1)]

$$A_{\mathbf{k}} = \Delta - F. \quad (\text{A9})$$

APPENDIX B

The general expression (34) for

$$\tilde{\Phi}_{i_1, \mathbf{k}_1; i_2, \mathbf{k}_2; \dots; i_{n-1}, \mathbf{k}_{n-1}; i_n}^{(n)}$$

takes the following forms in the particular cases of $n=0$:

$$\Phi^{(0)} = v_0 + \sum_i P_i V_i^{(1)} + \frac{1}{2} \sum_{i_1, i_2} \tilde{V}_{i_1, 0; i_2}^{(2)} P_{i_1} P_{i_2} - \frac{1}{2N} \sum_{i_1, i_2} \sum_{\mathbf{q}} \tilde{f}_{i, \mathbf{k}; j, -\mathbf{k}; i_1, \mathbf{q}; i_2}^{(4)} \|A_{\mathbf{q}}^{-1}\|_{i_2, i_1} \Big\}. \quad (\text{C1})$$

$$+ \frac{1}{6} \sum_{i_1, i_2, i_3} \tilde{V}_{i_1, 0; i_2, 0; i_3}^{(3)} P_{i_1} P_{i_2} P_{i_3} + \frac{1}{24} \sum_{i_1, i_2, i_3, i_4} \tilde{V}_{i_1, 0; i_2, 0; i_3, 0; i_4}^{(4)} P_{i_1} P_{i_2} P_{i_3} P_{i_4} + \dots, \quad (\text{B1})$$

$n=1$:

$$\Phi_i^{(1)} = V_i^{(1)} + \sum_{i'_1} P_{i'_1} \tilde{V}_{i'_1, 0; i}^{(2)} + \sum_{i'_1, i'_2} \frac{P_{i'_1} P_{i'_2}}{2} \tilde{V}_{i'_1, 0; i'_2, 0; i}^{(3)} + \sum_{i'_1, i'_2, i'_3} \frac{P_{i'_1} P_{i'_2} P_{i'_3}}{6} \tilde{V}_{i'_1, 0; i'_2, 0; i'_3, 0; i}^{(4)} + \dots, \quad (\text{B2})$$

$n=2$:

$$\Phi_{i_1, \mathbf{k}; i_2}^{(2)} = \tilde{V}_{i_1, \mathbf{k}; i_2}^{(2)} + \sum_{i'_1} P_{i'_1} \tilde{V}_{i'_1, 0; i_1, \mathbf{k}; i_2}^{(3)} + \sum_{i'_1, i'_2} \frac{P_{i'_1} P_{i'_2}}{2} \tilde{V}_{i'_1, 0; i'_2, 0; i_1, \mathbf{k}; i_2}^{(4)} + \dots, \quad (\text{B3})$$

$n=3$:

$$\Phi_{i_1, \mathbf{k}_1; i_2, \mathbf{k}_2; i_3}^{(3)} = \tilde{V}_{i_1, \mathbf{k}_1; i_2, \mathbf{k}_2; i_3}^{(3)} + \sum_{i'_1} P_{i'_1} \tilde{V}_{i'_1, 0; i_1, \mathbf{k}_1; i_2, \mathbf{k}_2; i_3}^{(4)} + \dots, \quad (\text{B4})$$

$n=4$:

$$\Phi_{i_1, \mathbf{k}_1; i_2, \mathbf{k}_2; i_3, \mathbf{k}_3; i_4}^{(4)} = \tilde{V}_{i_1, \mathbf{k}_1; i_2, \mathbf{k}_2; i_3, \mathbf{k}_3; i_4}^{(4)} + \dots. \quad (\text{B5})$$

APPENDIX C

Using the expression (50) for $f_{\text{ring}}^{\text{fluct}}$, we obtain

$$\begin{aligned} & \frac{1}{2} \sum_{i, j} \sum_{\mathbf{R}_1, \mathbf{R}_2} \left. \frac{\partial^2 f_{\text{ring}}^{\text{fluct}}}{\partial P_{i, \mathbf{R}_1} \partial P_{j, \mathbf{R}_2}} \right|_0 \delta P_{i, \mathbf{R}_1} \delta P_{j, \mathbf{R}_2} \\ &= \frac{k_B T}{2} \sum_{i, j} \sum_{\mathbf{k}} \frac{\delta \tilde{P}_{j, \mathbf{k}}^* \delta \tilde{P}_{i, \mathbf{k}}}{\sqrt{P_i(1-P_i)P_j(1-P_j)}} \\ & \times \left\{ A_{\mathbf{k}}^{ij} - \frac{1}{2} \frac{1-2P_i}{\sqrt{P_i(1-P_i)}} [I_{\mathbf{k}}^{ij} - \delta_{ij}] \frac{1-2P_j}{\sqrt{P_j(1-P_j)}} \right. \\ & - \frac{1-2P_j}{\sqrt{P_j(1-P_j)}} T_{\mathbf{k}}^{ij} - \frac{1}{2N} \sum_{i_1, i_2, i_3, i_4} \sum_{\mathbf{q}} \tilde{f}_{i_1, \mathbf{q}; -\mathbf{k}; i_2, -\mathbf{q}; i}^{(3)} \\ & \left. \times \|A_{\mathbf{q}}^{-1}\|_{i_2, i_3} \tilde{f}_{i_3, \mathbf{q}; i_4, \mathbf{k}-\mathbf{q}; j}^{(3)} \|A_{\mathbf{q}-\mathbf{k}}^{-1}\|_{i_4, i_1} \right\} \end{aligned}$$

From Eq. (54) one can derive the following relationships between $\delta \tilde{\mu}_{i, \mathbf{k}}$ and $\delta \tilde{P}_{j, \mathbf{k}}$:

$$\begin{aligned} & \frac{P_i(1-P_i)}{k_B T} \delta \tilde{\mu}_{i, \mathbf{k}} \\ &= \sum_j \frac{\delta \tilde{P}_{j, \mathbf{k}}}{\sqrt{P_j(1-P_j)}} \left\{ \frac{1-2P_j}{\sqrt{P_j(1-P_j)}} [\delta_{ij} - \|I_{\mathbf{k}}^{-1}\|_{ji}] \right. \\ & \left. + \sum_s \|I_{\mathbf{k}}^{-1}\|_{si} T_{\mathbf{k}}^{js} \right\}, \quad (\text{C2}) \end{aligned}$$

where $\delta \tilde{\mu}_{i, \mathbf{k}}$ is the Fourier transform of $\delta \mu_{i, \mathbf{R}}$,

$$\delta \mu_{i, \mathbf{R}} = \sum_{\mathbf{k}} \delta \tilde{\mu}_{i, \mathbf{k}} \exp(-i\mathbf{k}\mathbf{R}). \quad (\text{C3})$$

Taking into account Eq. (C2), we get

$$\begin{aligned} & \frac{1}{2} \sum_{i, j, l} \sum_{\mathbf{R}_1, \mathbf{R}_2, \mathbf{R}'} \left. \frac{\partial^2 f_{\text{ring}}^{\text{fluct}}}{\partial P_{i, \mathbf{R}_1} \partial P_{j, \mathbf{R}_2}} \frac{\partial \mu_{l, \mathbf{R}'}}{\partial P_{j, \mathbf{R}_2}} \right|_0 \delta P_{i, \mathbf{R}_1} \delta P_{j, \mathbf{R}_2} \\ &= \frac{k_B T}{2} \sum_{i, j} \sum_{\mathbf{k}} \frac{\delta \tilde{P}_{j, \mathbf{k}}^* \delta \tilde{P}_{i, \mathbf{k}}}{\sqrt{P_i(1-P_i)P_j(1-P_j)}} \\ & \times \left\{ \frac{1}{2} \frac{1-2P_i}{\sqrt{P_i(1-P_i)}} [I_{\mathbf{k}}^{ij} + \|I_{\mathbf{k}}^{-1}\|_{ij} - 2\delta_{ij}] \frac{1-2P_j}{\sqrt{P_j(1-P_j)}} \right. \\ & + \frac{1-2P_j}{\sqrt{P_j(1-P_j)}} \left[T_{\mathbf{k}}^{ij} - \sum_s T_{\mathbf{k}}^{is} \|I_{\mathbf{k}}^{-1}\|_{sj} \right] \\ & \left. + \frac{1}{2} \sum_{l, s} T_{\mathbf{k}}^{il} T_{-\mathbf{k}}^{js} \|I_{\mathbf{k}}^{-1}\|_{ls} \right\}. \quad (\text{C4}) \end{aligned}$$

Substituting Eqs. (C1) and (C4) into Eq. (84), we arrive at Eq. (85) (see Sec. VIII).

APPENDIX D

In this appendix, we present the expressions for the Fourier transforms $\tilde{V}_{i, \mathbf{k}; j}^{(2)}$, $\tilde{V}_{l, 0; i, \mathbf{k}; j}^{(3)}$, and $\tilde{V}_{l, 0; m, 0; i, \mathbf{k}; j}^{(4)}$ of the mixing potentials through its values in the direct space, which are necessary for calculations of the phase diagrams within the ring approximation performed in Sec. XIII.

It is convenient to present the general expression (30) at $n=2$ in the following form:

$$\tilde{V}_{i, \mathbf{k}; j}^{(2)} \equiv \sum_{\mathbf{R}} V_{i, \mathbf{R}; j, 0}^{(2)} \exp[-i\mathbf{k}\mathbf{R}] = \sum_{s=1}^{\infty} V_s^{(2)} Z_{i, \mathbf{k}; j}^{(s)}, \quad (\text{D1})$$

where

$$Z_{i, \mathbf{k}; j}^{(s)} = \sum_{\mathbf{R}_j^{(s)}} \exp[-i\mathbf{k}\mathbf{R}_j^{(s)}], \quad Z_{j, \mathbf{k}; i}^{(s)} = Z_{i, -\mathbf{k}; j}^{(s)}, \quad (\text{D2})$$

$\mathbf{R}_{ij}^{(s)}$ are the radius vectors connecting two unit cells in which, respectively, i th and j th sites are separated by the distance of s th coordination shell. $\mathbf{R}_{ij}^{(s)}$ can be equal to zero in the case where such i th and j th sites belong to the same unit cell. When a four-site unit cell is chosen as a cube of fcc crystal lattice (see Fig. 2), for $s=1,2$ we have

$$Z_{i,\mathbf{k};i}^{(1)} = 0,$$

$$Z_{1,\mathbf{k};2}^{(1)} = \exp[-ia(k_x + k_y)/2]Z_{xy},$$

$$Z_{1,\mathbf{k};3}^{(1)} = \exp[-ia(k_x + k_z)/2]Z_{xz},$$

$$Z_{1,\mathbf{k};4}^{(1)} = \exp[-ia(k_y + k_z)/2]Z_{yz},$$

$$Z_{2,\mathbf{k};3}^{(1)} = \exp[-ia(-k_y + k_z)/2]Z_{yz},$$

$$Z_{2,\mathbf{k};4}^{(1)} = \exp[-ia(-k_x + k_z)/2]Z_{xz},$$

$$Z_{3,\mathbf{k};4}^{(1)} = \exp[-ia(-k_x + k_y)/2]Z_{xy}, \quad (\text{D3})$$

$$Z_{i,\mathbf{k};j}^{(2)} = \delta_{ij}2[\cos(ak_x) + \cos(ak_y) + \cos(ak_z)], \quad (\text{D4})$$

where

$$Z_{xy} = 2\{\cos[a(k_x + k_y)/2] + \cos[a(k_x - k_y)/2]\},$$

$$Z_{xz} = 2\{\cos[a(k_x + k_z)/2] + \cos[a(k_x - k_z)/2]\},$$

$$Z_{yz} = 2\{\cos[a(k_y + k_z)/2] + \cos[a(k_y - k_z)/2]\}, \quad (\text{D5})$$

k_x, k_y, k_z are the Cartesian coordinates of \mathbf{k} in units of $2\pi/a$ (a is the lattice parameter). One can also obtain that

$$\tilde{V}_{l,\mathbf{0};i,\mathbf{k};j}^{(3)} = \begin{cases} 2V_{s=1}^{(3)}Z_{i,\mathbf{k};j}^{(s=1)} & \text{if } l \neq i \neq j \\ 0 & \text{otherwise,} \end{cases} \quad (\text{D6})$$

$$\tilde{V}_{l,\mathbf{0};m,\mathbf{0};i,\mathbf{k};j}^{(4)} = \begin{cases} 2V_{s=1}^{(4)}Z_{i,\mathbf{k};j}^{(s=1)} & \text{if } l \neq m \neq i \neq j \\ 0 & \text{otherwise,} \end{cases} \quad (\text{D7})$$

where the triplet $V_{s=1}^{(3)}$ and quadruplet $V_{s=1}^{(4)}$ atomic interactions for only first corresponding coordination shells are taken into account. It should be noted that in the above-written expressions we impose the symmetry of the *disordered* state on the mixing potentials. Thus, we do not take into account the structural dependence of the mixing potentials.²¹

In conclusion let us write down the following symmetry property of the mixing potentials, which was not obtained in Ref. 21 and which is a generalization of the one presented in Eq. (9.5) of Ref. 17 to the case of presence of sublattices:

$$\begin{aligned} \tilde{V}_{i_1,\mathbf{k}_1;i_2,\mathbf{k}_2;\dots;i_{n-1},\mathbf{k}_{n-1};i_n}^{(n)} \\ = \tilde{V}_{i_1,\mathbf{k}_1;i_2,\mathbf{k}_2;\dots;i_{t-1},\mathbf{k}_{t-1};i_n} \\ - \sum_{p=1}^{n-1} \mathbf{k}_p;i_{t+1},\mathbf{k}_{t+1};\dots;i_{n-1},\mathbf{k}_{n-1};i_t \end{aligned} \quad (\text{D8})$$

($t=1,2,\dots,n-1$). Note the interchange of the positions of i_t and i_n in Eq. (D8). This property was used at derivation of the expressions in Secs. VII and VIII. The proof of the property is similar to that one in Sec. 9 of Ref. 17. From the definition (34) it follows that the functions $\tilde{\Phi}_{i_1,\mathbf{k}_1;i_2,\mathbf{k}_2;\dots;i_{n-1},\mathbf{k}_{n-1};i_n}^{(n)}$ also have the symmetry property (D8).

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