Master equation approach to the theory of diffusion in alloys and calculations of enhancement factors for tracer solvent and tracer solute diffusion in FCC alloys

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Abstract The earlier-suggested master equation approach is used to develop the consistent statistical theory of diffusion in substitution alloys using the five-frequency model of FCC alloys as an example. Expressions for the Onsager coefficients in terms of microscopic interatomic interactions and some statistical averages are presented. We discuss methods of calculations of these averages using various statistical approximations and both the nearest-neighbor and the second-shell approximations to describe the vacancy correlation effects. The methods developed are used for calculations of enhancement factors for tracer solvent and tracer solute diffusion in dilute FCC alloys. We show that some significant contribution to the tracer solvent enhancement factor related to the thermodynamic activity of vacancies was missed in the previous treatments of this problem. It implies that the most of existing estimates of parameters of five-frequency model for real alloys should be revised. For the tracer solute diffusion, the enhancement factor seems to be calculated for the first time. The results obtained are used to estimate the microscopic parameters important for diffusion, including the vacancy-solute interaction, in several FCC alloys for which necessary experimental data are available.

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I. INTRODUCTION

Microscopic theories of diffusion in alloys can be divided into two main groups: (i) those based on the random walk theory and the “vacancy-solute association-dissociation” models (to be called “traditional” theories) \cite{1–9} and (ii) those based on the master equation approach recently suggested by Nastar et al. \cite{10–12}. The traditional approaches described in a number of reviews and textbooks \cite{6, 8, 9} put grounds for the present microscopic understanding of diffusion. However, the results of these approaches are exact only in the dilute alloy limit when the site fractions of solute, \(c\), tend to zero, while extensions of these approaches to the finite \(c\) meet difficulties. Even for a dilute binary alloy \(AB\) with low \(c_B \ll 1\), calculations of enhancement factors, that is, the linear in \(c_B\) terms in diffusion coefficients, for both the tracer solute and the chemical (intrins ic) diffusion seem to be not performed, while traditional calculations of the tracer solvent enhancement factor, as discussed by Nastar \cite{11} and below, include significant inaccuracies.

The master equation approach (MEA) to the steady-state diffusion theory suggested by Nastar et al. \cite{10–12} can be used for both the dilute and the concentrated alloys. It can be formulated in terms of fully microscopic notions, such as the “saddle-point”, “kinetic” and “configurational” interactions described below which can be calculated by \textit{ab initio} methods, see, e. g., \cite{13}. Nastar et al. \cite{10} used MEA to study some general features of diffusion in concentrated alloys, and the results (obtained using rather simple approximations) reasonably agree with Monte Carlo simulations. Nastar \cite{11} used this approach to study the long-discussed problem of calculating the tracer self-diffusion enhancement factor, and her results agree with the Monte Carlo simulations better than the traditional ones \cite{2, 4, 7}. Barbe and Nastar \cite{12} generalized the “pairwise effective interaction” version of MEA used in \cite{10, 11} to study features of diffusion in alloys with a high ratio of solute-vacancy to solvent-vacancy exchange frequencies.

At the same time, the formulation of MEA given in Refs. \cite{10–12} includes a number of shortcomings which prevent from further applications of this approach. First, even the most detailed paper \cite{11} does not contain explicit expressions for the basic quantity of the theory, the vacancy-atom exchange probability, which hinders understanding and generalizations of the method. Second, basic equations in \cite{11} are implicit and cumbersome, and it is difficult to use them. Third and most important, treatment of vacancy-solute interactions in Ref. \cite{11} includes inaccuracies which are manifested, in particular, in the disagreement of one of results in \cite{11} with that of traditional theories, as discussed below in Sec. VC.

In this work we present a new formulation of the master equation approach free from the shortcomings mentioned, and use it to calculate the enhancement factors for tracer diffusion in dilute FCC alloys. Our equations are explicit and simple, they can be solved using the standard methods of statistical physics, and their possible generalizations (for example, to the case of not-nearest or non-pairwise interactions) are evident.

To be definite, we illustrate our approach by consideration of dilute FCC alloys using the pairwise nearest-neighbor interaction model which is commonly called “the five-frequency model” \cite{1–9}. At the same time, we also take into account the solute-solute interactions not considered in the standard five-frequency model.

The important general feature of our approach is the proper description of effects of the vacancy-solute interac-
tion (or “vacancy-solute binding energy” \[1\]) in particular, for the tracer self-diffusion enhancement factor \(b_{\text{A}^*}\). We show that all previous calculations of \(b_{\text{A}^*}\) using both the traditional methods \[2, 4, 7\] and the version of MEA used in \[11\], missed the contribution of thermodinamic activity of vacancies related to the vacancy-solute interaction. This led to spreading of a pessimistic opinion that the “diffusion experiments by themselves are not sufficient to determine this binding energy” \[9\], and presently experimental estimates of this energy use various plausible models with no consistent statistical justification \[11–13\]. Our results show that this pessimistic opinion is wrong, and the consistent estimates of \(\nu^{\nu B}\) for several alloys using available experimental data are presented in this work. These results also imply that the most of existing estimates of parameters of five-frequency model (“frequency ratios”) for real alloys \[8, 9\] should be revised.

The paper is organized as follows. In Sec. \[II\] we present main equations of the master equation approach. In Sec. \[III\] these equations are used to derive general expressions for Onsager coefficients which describe the steady-state diffusion in a substitution alloy. Here we use the methods suggested by Nastar et al. \[10–12\] but employ our explicit formulation of the master equation approach. In Sec. \[IV\] we discuss both exact relations and methods of approximate calculations for statistical averages which enter into the general expressions for Onsager coefficients. In Sec. \[V\] we present explicit expressions for Onsager and diffusion coefficients in a binary alloy at any concentration and show that in the case of a dilute alloy, these expressions coincide with those of the traditional theory \[8\]. In Sec. \[VI\] and \[VII\] we discuss the enhancement factor for diffusion of tracer solvent and tracer solute, respectively. In Sec. \[VIII\] we estimate parameters of the five-frequency model and interactions significant for diffusion for several alloys for which necessary experimental data are available. We also find that the description of these data by the five-frequency model seems to be physically reasonable. Our main conclusions are summarized in Sec. \[IX\].

II. GENERAL EQUATIONS OF DIFFUSIONAL KINETICS IN SUBSTITUTION ALLOYS

Basic equations of the master equation approach for the diffusional kinetics of substitution alloys have been derived earlier \[14, 15\]. Below we present the necessary relations from Ref. \[18\]. We consider a substitution alloy with \((m+1)\) components \(p^\prime\) which include host atoms denoted by index \(h\), solute atoms denoted by Greek letters \(\alpha, \beta, \lambda, \mu, \nu\), and vacancies denoted by \(v\). Latin letters \(p, q, r\) will denote all kinds of atoms, both \(h\) and \(\alpha\), while Greek letters \(\rho, \sigma, \tau\) will denote both solute atoms \(\alpha\) and vacancies \(v\), thus the whole set \(p^\prime\) can be written either as \(\{p, v\}\) or as \(\{h, \rho\}\). Distinctions of atoms over lattice sites \(i\) are described by the different occupation number sets \(\{n_i^p\}\) where the operator \(n_i^p\) is 1 when the site \(i\)

\[
n_i^h = \left(1 - \sum_{\rho} n_i^\rho\right). \tag{1}
\]

This is convenient to describe real alloys where the vacancy site fraction is very low: \(\langle n_i^v \rangle \ll \langle n_i^\rho \rangle\), while Nastar et al. \[10–12\] eliminate vacancy occupation operators \(n_i^v\) in their calculations for statistical averages which enter into the configurational interaction \(W_{ij}\) in the master equation approach. In Sec. \[IV\] we discuss both exact relations and methods of approximate calculations for statistical averages which enter into the general expressions for Onsager coefficients. In Sec. \[V\] we present explicit expressions for Onsager and diffusion coefficients in a binary alloy at any concentration and show that in the case of a dilute alloy, these expressions coincide with those of the traditional theory \[8\]. In Sec. \[VI\] and \[VII\] we discuss the enhancement factor for diffusion of tracer solvent and tracer solute, respectively. In Sec. \[VIII\] we estimate parameters of the five-frequency model and interactions significant for diffusion for several alloys for which necessary experimental data are available. We also find that the description of these data by the five-frequency model seems to be physically reasonable. Our main conclusions are summarized in Sec. \[IX\].
where $\omega_{pv}$ is the attempt frequency (which has the order of magnitude of a mean frequency of vibrations of a jumping atom in an alloy), and $\Delta S_{\text{SP}}^{\text{pp}}$ is the entropy difference between the saddle-point and initial alloy states.

The saddle point energy $\hat{E}_{\text{SP}, i,j}^{\text{pp}}$ in (7) depends in general on the atomic configuration near the $ij$ bond. We describe this dependence by the pairwise interaction model [13, 18] and write this energy as follows:

$$\hat{E}_{\text{SP}, i,j}^{\text{pp}} = E_h^p + \sum_{\lambda l} \Delta_{\lambda p,i,j}^{\text{li}} \eta_{\lambda j}^i, \quad \Delta_{\lambda p,i,j}^{\text{li}} = (\varepsilon_{p,i,j}^{\lambda} - \varepsilon_{p,j,i}^{\lambda}). \quad (9)$$

Here $E_h^p$ is the saddle point energy for a $p$-species atom in the pure host metal, the parameter $\Delta_{\lambda p,i,j}^{\text{li}}$ (to be called the “saddle-point interaction”) describes changes in this energy due to a possible substitution of a host atom in site $l$ by a $\lambda$-species solute atom, while $\varepsilon_{p,i,j}^{\lambda}$ and $\varepsilon_{p,j,i}^{\lambda}$ are microscopic parameters which can be calculated using either $ab$ initio [13] or model [18] calculations.

The most general expression for the probability $P$ in (3) can be written as [10, 17]

$$P\{n_i^p\} = \exp \left[ \beta \left( \Omega + \sum_{\rho} \lambda_i^{\rho p} n_i^{\rho p} - H_{\text{int}} - \hat{h}_{\text{int}} \right) \right] \quad (10)$$

$$\hat{h}_{\text{int}} = \frac{1}{2} \sum_{\rho \sigma, ij} h_{ij}^{\rho \sigma} n_i^{\rho p} n_j^{\sigma p} + \frac{1}{6} \sum_{\rho \sigma \tau, ijk} h_{ij}^{\rho \sigma \tau} n_i^{\rho p} n_j^{\sigma p} n_k^{\tau p} + \ldots \quad (11)$$

Here parameters $\lambda_i^{\rho}$ (which are both time- and space-dependent, in general) can be called “site chemical potentials” for an $\alpha$-species atom or a vacancy with respect to a host atom. These parameters are related to the local chemical potentials $\mu_i^{\alpha}$ and $\mu_i^{\beta}$ as [22]:

$$\lambda_i^{\rho} = (\mu_i^{\alpha} - \mu_i^{\beta}). \quad (12)$$

Quantities $h_{ij}^{\rho \sigma}$ in (11) (to be called “effective interactions”) [10, 12] describe renormalizations of configurational interactions [3] in the course of kinetic processes, and they can depend on both time and space, too. Constant $\Omega$ is determined by normalization.

Multiplying Eq. (4) by operators $n_i^{\rho}$ and summing over all configurations $\{n_i^{\rho}\}$, we obtain equations for the mean occupations of site (“local site fractions”) $c_i^{\rho} = \langle n_i^{\rho} \rangle$:

$$dc_i^{\rho} / dt = \langle n_i^{\rho} \hat{S} \rangle \quad (13)$$

where $\langle \ldots \rangle$ means averaging over distribution (10), e.g.:

$$c_i^{\rho} = \langle n_i^{\rho} \rangle = \sum_{\{n_i^{\rho}\}} n_i^{\rho} P\{n_i^{\rho}\}. \quad (14)$$

For simplicity, in this work we consider the case of presence in (11) of only pairwise effective interactions $h_{ij}^{\rho \sigma}$ which is sufficient for dilute alloys while, non-pairwise effective interactions will be discussed elsewhere. Then after some manipulations described in detail in [18], Eqs. (15)-(17) can be written similarly to Eqs. (I-28)-(I-34):

$$dc_i^{\rho} / dt = \sum_{j(i)} \left\{ \langle \gamma_{\alpha \beta} \delta_{\rho p} \rangle \left[ \exp \left[ \beta \left( \lambda_i^{\rho} + \lambda_j^{\rho} - h_{ij}^{\rho \sigma} \right) - \sum_{\lambda l} (\alpha^{\lambda \alpha} + \beta^{\lambda \beta} n_l^{\lambda}) \right] - \{i \to j\} \right] \right\}$$

$$- \{i \to j\}. \quad (15)$$

where we also correct some misprints made in [18] and use the identity $\langle c_i^{\rho} + \sum_{\alpha} n_{\alpha i}^{\rho} \rangle = 1 + \langle c_i^{\rho} \rangle$. In Eqs. (15), symbol $j(i)$ means summation over sites $j$ being nearest neighbors of site $i$, and the factor $\gamma_{\rho p}$ can be called “the activation frequency” for a $p \to \rho$ exchange in a pure host metal which can be written similarly to (7):

$$\gamma_{\rho p} = \omega_{pv}^{\rho \rho} \exp (-\beta E_{\rho \rho}^{\rho \rho}). \quad (16)$$

Eqs. (15)-(17) show that the operator $\hat{b}_{ij}^{\rho}$ in (13) is given by Eq. (I-33):

$$\hat{b}_{ij}^{\rho} = n_i^{\rho} n_j^{\rho} \hat{b}_{ij}^{\rho} \exp \left[ \sum_{\alpha} \beta (u_{\alpha i}^{\rho} + u_{\alpha j}^{\rho}) n_{\alpha i}^{\rho} - \sum_{\alpha} \beta \Delta_{\alpha p,i,j}^{\rho} n_{\alpha i}^{\rho} \right] \quad (17)$$

where $\Delta_{\alpha p,i,j}^{\rho}$ is the same as in Eq. (9), while parameters $u_{\alpha i}^{\rho}$ (to be called “kinetic interactions” [19]) are expressed via $V_{ij}^{\alpha \rho}$ in (2) as follows:

$$u_{\alpha i}^{\rho} = \langle V_{i\alpha}^{\rho} - V_{i\beta}^{\rho} \rangle. \quad (18)$$

Eqs. (15)-[17] show that the operator $\hat{b}_{ij}^{\rho}$ describes influence of neighboring solute atoms on the probability of a $p \to \rho$ jump. Note that the kinetic interaction $u_{\alpha i}^{\rho}$ in (17) and (18) does not depend on the kind $\rho$ of a jumping atom, unlike the saddle-point interaction $\Delta_{\alpha p,i,j}^{\rho}$ in (9).

Using the operator identities

$$n_i^{\rho} n_j^{\beta} = n_i^{\rho} \delta_{\rho \beta}, \quad \exp(x n_i^{\rho}) = 1 + n_i^{\rho} f(x) \quad (19)$$

where $f(x)$ is $(e^x - 1)$ and $\delta_{\rho \beta}$ is the Kroneker symbol, we can explicitly write the operator $\hat{b}_{ij}^{\rho}$ [17] as follows:

$$\hat{b}_{ij}^{\rho} = n_i^{\rho} n_j^{\rho} \prod_l (1 + f_{\alpha p,\Delta_l, ij}^{\rho} n_l^{\alpha}), \quad (20)$$

$$f_{\alpha p,\Delta_l, ij}^{\rho} = [\exp(\beta \Delta_{\alpha p,i,j}^{\rho} - \beta u_{\alpha i}^{\rho} - \beta u_{\alpha j}^{\rho}) - 1]. \quad (21)$$

Finally, we make remarks on the difference between our formulation of the master equation approach and that used by Nastar [11]. First, our formulation is based on the explicit expression (7) for the inter-site atomic exchange probability $W_{ij}^{\rho \rho}$. On the contrary, Nastar treats
this $W_{ij}^{pv}$ as some unknown operator and estimates averages with this operator for dilute alloys using some indirect considerations rather than the direct calculations. For concentrated alloys, she mentions “difficulties” to construct $W_{ij}^{pv}$ “satisfying the detailed balance principle”, while this principle is ideally obeyed for our expression \(^7\). As the result, Ref. \(^11\) does not contain explicit equations \(^15\) for time derivatives $d\hat{c}_{ij}^p/dt$ which include, in particular, the vacancy activity factor exp ($\beta\lambda_j^v$) discussed below. Second, the above-mentioned elimination by Nastar et al. \(^10\)\(^12\) of vacancy occupation operators $n_i^z$ [rather than operators $n_i^z$ in Eq. \(^11\)] can lead to difficulties in practical calculations, for example, in the ab initio calculations of interactions \(^5\) by standard methods \(^13\). Such difficulties are absent in our formulation based on Eqs. \((11)\)\(^\sim\)(20).

**III. GENERAL EQUATIONS FOR ONSAGER COEFFICIENTS**

**A. Method of calculations of Onsager coefficients in the master equation approach**

The steady-state diffusion is commonly described in terms of Onsager coefficients $L_{pq}$ which relate the atomic flux density $J_p$ to the chemical potential gradients $\nabla \mu_q$ supposed to be small and constant \(^8\). These chemical potentials can be counted off the vacancy chemical potential $\mu_v$, and in the cubic metals where diffusion is isotropic, Onsager relations can be written as:

$$J_p = \sum_q L_{pq} \nabla \mu_q$$ \(^22\)

where $\mu_{qv}$ is $(\mu_q - \mu_v)$. In a nonuniform alloy, local values $\mu_i^{pv}$ are related to $\lambda_i^v$ defined by Eqs. \((12)\) as follows:

$$\mu_i^{pv} = (\lambda_i^v - \lambda_v^v), \quad \mu_i^{pv} = -\lambda_v^v.$$ \(^23\)

Below we use the methods of calculations of Onsager coefficients developed by Nastar et al. \(^10\)\(^12\). The steady-state diffusion corresponds to a weakly nonuniform alloy for which the local chemical potential difference $\delta \lambda_{ji} = (\lambda_i^v - \lambda_j^v)$ in Eqs. \((15)\) is small, while effective interactions $h_{ij}^{\alpha \beta}$ (for brevity, to be called also “fields”) are proportional to these differences. Linearizing Eqs. \((15)\) in $\delta \lambda_{ji}$ and $h_{ij}^{\alpha \beta}$ and expressing $\delta \lambda_{ji}$ via $\delta \mu_{ji}^{pv} = (\mu_{ji}^{pv} - \mu_{ji}^{pv})$ according to \((22)\), we obtain:

$$d\hat{c}_{ij}^p/dt = \beta \sum_{j(i)} \left\{ \gamma_{ji} \exp (\beta \lambda_{ji} + \lambda_{ji}) \hat{\mu}_{ji}^p \times \left[ \delta \mu_{ji}^{pv} (h_{ji}^{pv} - h_{ji}^{pv}) - \sum_{\lambda l} (h_{ji}^{\lambda \lambda} - h_{ji}^{\lambda \lambda}) n_i^l \right] + \sum_{\lambda l} (h_{ji}^{l \lambda} - h_{ji}^{l \lambda}) n_i^l \right\}.$$ \(^24\)

Here and below, $\lambda_{ji}$ or $\lambda_{ji}$ without a site index $i$ or $j$ means the equilibrium value of this chemical potential, while averaging is made over the equilibrium distribution $P$ described by Eq. \((10)\) with $\lambda_0^p = \lambda_p$ and $h_{int} = 0$. In accordance with the definition \((11)\), fields $h_{ij}^{\alpha \beta}$ are nonzero only when index $p$ corresponds to a solute atom $\alpha$, while $h_{ij}^{\alpha \beta} = 0$ [which is also illustrated by Eqs. \((15)\)]. For the given $j$, each term in the right-hand side of \((24)\) has evidently the meaning of an atomic flux $h_{ij}^{p}$ through bond $ij$. It enables us to write the linear relation between these fluxes and quantities $\hat{\mu}_{ji}^{pv}$ and $h_{ij}^{\alpha \beta}$ in \((24)\). It was also noted in \((10)\)\(^\sim\)(11) that for the steady-state diffusion when the left-hand side of Eqs. \((24)\) vanishes, effective interactions $h_{ij}^{\alpha \beta}$ are antisymmetric in indices $i$ and $j$:

$$h_{ij}^{\alpha \beta} = -h_{ji}^{\alpha \beta}, \quad h_{ji}^{\alpha \beta} = -h_{ij}^{\alpha \beta}.$$ \(^25\)

Denoting also site $i$ by index “0” and site $j$ by index “1”, we can write the above-mentioned fluxes $J_{0\rightarrow1}^p$ as follows:

$$J_{0\rightarrow1}^p = -\beta \left\{ \hat{\mu}_p (\delta \mu_{0v} + 2h_{1v}^{pv}) - \sum_{\lambda l} (h_{0l}^{\lambda \lambda} - h_{0l}^{\lambda \lambda} + h_{1l}^{\lambda \lambda} + h_{1l}^{\lambda \lambda}) \right\}$$ \(^26\)

where $\delta \mu_{pv}$ is $(\mu_{0}^{pv} - \mu_{1}^{pv})$, $h_{1v}^{pv}$ is the nearest-neighbor effective interaction, and $\hat{\mu}_p$ and $l_{0l}^{hl}$ are statistical averages:

$$\hat{\mu}_p = \langle \hat{\mu}_p \rangle_0, \quad l_{0l}^{hl} = \langle \hat{w}_{0l} n_i^l \rangle.$$ \(^27\)

Here the operator $\hat{w}_{0l}^{p}$ is the product of the operator $\hat{b}_{0l}^p$ given by Eq. \((17)\) or \((20)\) and the constant factor $\Gamma_p$ which enters into Eqs. \((24)\):

$$\hat{w}_{0l}^p = \Gamma_p \hat{b}_{0l}^p.$$ \(^28\)

Fields $h_{ij}^{p}$ in Eqs. \((24)\) can be found from the stationarity condition for two-site averages \((10)\)\(^\sim\)(11):

$$\frac{d}{dt} \langle n_i^\alpha n_j^\beta \rangle = 0$$ \(^30\)

which yields the following equations for $h_{ij}^{p}$ \((10)\)\(^\sim\)(17):

$$\sum_{k \neq 0 \neq j} \left[ m_{\alpha,\beta,\gamma}^{p,kl} (\delta \mu_{kl}^{\alpha \gamma} + 2h_{0k}^{\alpha \gamma}) - \sum_{\lambda l} m_{\alpha,\beta,\gamma}^{\lambda,kl} (h_{0l}^{\lambda \lambda} - h_{kl}^{\lambda \lambda}) - h_{0l}^{\lambda \lambda} - h_{kl}^{\lambda \lambda} + m_{\alpha,\beta,\gamma}^{\alpha,kl} (\delta \mu_{kl}^{\alpha \gamma} + 2h_{0k}^{\alpha \gamma}) \right] = 0$$ \(^31\)

where

$$m_{\alpha,\beta,\gamma}^{p,kl} = \langle \hat{w}_{ik}^{p} n_j^\gamma n_k^\lambda \rangle, \quad m_{\alpha,\beta,\gamma}^{\alpha,kl} = \langle \hat{w}_{ik}^{p} n_j^\gamma n_k^\lambda \rangle.$$ \(^32\)

Following Nastar \(^11\), we consider diffusion along z-axis of an FCC alloy when chemical potentials $\mu_i^p = \mu_i^p (R_i)$ depend only on $z_i$. Let us denote positions of sites 0 and 1 in Eqs. \((26)\) as $R_0 = (0, 0, 0)$ and $R_1 = \ldots$, and
(0, a₀/2, a₀/2) where a₀ is the FCC lattice constant, while different sites near the bond (0,1) are numbered as shown in Fig. 1. Quantity δμₚᵥ in Eqs. (26) is the difference of chemical potentials between neighboring atomic planes along z axis: δμₚᵥ = μₚᵥ(0,0,a₀/2) - μₚᵥ(0,0,0).

The field hⁿρₚ = hⁿρλ(Rₚ₀) does not change under rotations of vector Rₚ₀ = (x₀ₚ, y₀ₚ, z₀ₚ) around z-axis, and this field changes its sign under reflection with respect to (x, y)-plane: \( hⁿρλ(x₀ₚ, y₀ₚ, -z₀ₚ) = -hⁿρλ(x₀ₚ, y₀ₚ, z₀ₚ) \). For brevity, we denote the set of crystallographically equivalent sites with the same positive value z₀ₚ > 0 as \( Iₙ⁺ \), the similar set with the negative value z₀ₚ = -zₚ, as \( Iₙ⁻ \), and the fields \( hⁿρλ(Rₚ₊ₙ) \) or \( hⁿρλ(Rₚ₋ₙ) \) which correspond to the set of sites \( Iₙ⁺ \) or \( Iₙ⁻ \), as \( hⁿρλ \) or \( -hⁿρλ \). Index \( n \) which numbers different sets of equivalent sites, \( Iₙ⁺ \) and \( Iₙ⁻ \), is supposed to increase with the distance \( |Rₚ₀| \), and for a given \( |Rₚ₀| \), it increases with the \( z₀ₚ \) value. Thus \( n = 1 \) corresponds to the nearest-neighbor field \( h₁ = h(Rₚ₀) \), and Eqs. (26) can be concisely written as:

\[
Jₚⁿ⁻⁻ₙ⁺ = -β \left[ \sum \frac{hⁿρλ}{2} + \sum \lambda \sum n_{max} (hⁿλ - hⁿρλ) \right].
\] (33)

Here \( n_{max} \) is the maximum number of fields \( hⁿρλ \) taken into account, and increase of \( n_{max} \) corresponds to a more accurate description of vacancy correlation effects [10]. Coefficients \( hⁿλ \) and \( hⁿρλ \) in (33) are defined as follows:

\[
\lambda \rho \sum n_{max} \left( \hat{w}³ = \frac{\lambda}{\rho λ} \right), \quad \lambda \rho \sum n_{max} \left( \hat{w}³ = \frac{\lambda}{\rho λ} \right).
\] (34)

Here index \( n \) at brackets means that it should be put at each term within brackets, e. g. \( (n₁₊⁻ + \ldots) \lambda = (n₂₊⁻ + \ldots) \lambda \), and the following notation is used:

\[
n₁₊⁻ = n(Rₚ₊₁), \quad n₂₊⁻ = n(Rₚ₊₂ + R₁).
\] (35)

Employing the same notation as in (33), we can concisely write Eqs. (31) and (32) similarly to (33):

\[
mⁿρₚᵥ = \sum_{i,j} \left[ (hⁿρλ - hⁿρλ) \right] + \left[ (hⁿρλ - hⁿρλ) \right] = 0
\] (36)

where coefficients \( tⁿλ \) and \( mⁿρₚᵥ \) are defined as follows:

\[
tⁿλ = \sum_{k=1}^{12} \left( \hat{w}³ = \frac{\lambda}{\rho λ} \right), \quad mⁿρₚᵥ = \sum_{k=1}^{12} \left( \hat{w}³ = \frac{\lambda}{\rho λ} \right).
\] (37)

Here \( n₁₊⁻ \) and \( n₂₊⁻ \) are the same as in (31); the operator \( nⁿρₚᵥ \) corresponds to the vector \( Rₚ₀ \) chosen as “the first one” in the set of vectors \( Rₚ₀ ; n₁₊⁻ \) defined similarly to \( n₁₊⁻ \) in Eq. (35) is \( n(Rₚ₊₁ + R₁) \); and we took into account the symmetry or antisymmetry of each average in (36) with respect to reflections \( Rₚ₋₁ \rightarrow (Rₚ₋₁) \).

Eqs. (36) enable us to express all fields \( hⁿρλ \) as linear combinations of \( δμₚᵥ \). Then substitution of these expressions into Eqs. (35) yields the linear relation between the flux \( Jₚⁿ⁻⁻ₙ⁺ \) and differences \( δμₚᵥ \):

\[
Jₚⁿ⁻⁻ₙ⁺ = \sum_q Aₚₚ δμₚᵥ
\] (38)

where parameters \( Aₚₚ \) are some functions of coefficients \( tⁿρλ, mⁿρₚᵥ \) and \( tⁿρλ \) in Eqs. (36). To relate parameters \( Aₚₚ \) in (38) to Önsager coefficients \( Lₚₚ \) in (22) we note that the flux density \( Jₚ \) along z axis can be found as the ratio of the total flux through one site lying in the plane (0,0,0) to the area \( S = a₀²/2 \) corresponding to each site in that plane, while the difference \( δμₚᵥ \) in Eq. (38) is simply expressed via \( \muₚᵥ = (0,0,0,0,0) \):

\[
Jₚ = 4Jₚⁿ⁻⁻ₙ⁺ / S = 8Jₚⁿ⁻⁻ₙ⁺ / a₀²
\] (39)

\[
δμₚᵥ = (dμₚᵥ / dz) a₀² / 2
\] (40)

Substituting these relations into (38) and comparing the result with a \( z \)-component of Eq. (22), we find:

\[
Lₚₚ = -4Aₚₚ / a₀ = -na₀² \hat{Aₚₚ}
\] (41)

where \( n = 4/a₀² \) is the atomic density in the FCC lattice.

### B. Model of the nearest-neighbor kinetic and saddle-point interactions

Below we consider the model when both the saddle-point and kinetic interactions, \( Δµ₁ / dz \) and \( u₁ / dz \) in Eqs. (17), (20) and (21), are nonzero only for the nearest-neighbors. This corresponds to the standard “five-frequency model” for FCC alloys [1-9]. For this model, the operator \( \hat{w}³ \) in Eqs. (31) and (32) takes the form:

\[
\hat{w}³ = \frac{\lambda}{\rho λ} \prod \lambda (1 + \sum_{m=1}^{12} \sum_{n=1}^{max} \left( (hⁿρλ - hⁿρλ) \right) \prod \left( (1 + \sum_{n=1}^{max} \left( (hⁿρλ - hⁿρλ) \right) \right)
\] (42)

where sites \( m \) and \( l \) are numbered as shown in Fig. 1. In this figure, sites with positions \( R_k \) for \( k \) between 1 and 12 correspond to the nearest neighbors of site “0” positioned at \( R₀ \), while sites positioned at \( R_k = \hat{R}_k = \hat{R}_k = \hat{R}_k = \hat{R}_k = \hat{R}_k = \hat{R}_k = \hat{R}_k \) correspond to the nearest neighbors of site “1” with \( \hat{R}_k = (0, a₀/2, a₀/2) \). The relations

\[
\tilde{r} = 0, \quad \tilde{q} = 9, \quad \tilde{r} = 12, \quad \tilde{t} = 2, \quad \tilde{t} = 4
\] (43)

are also taken into account.

In Eq. (42), index \( l \) in the first product takes four values: 2, 4, 9 or 12 which correspond to the nearest neighbors of bond (0,1), i. e. of both site 0 and site 1. Index \( m \) in the second product corresponds to the nearest
neighbors of only one of these sites, site 0 or site 1, and takes fourteen values: 3, 5, 6, 7, 8, 10, 11, 1, 2, 3, 4, 5, 9 or 12. Quantity \( f_{\Delta}^{\mu} \) or \( f_{\nu}^{\mu} \) in Eq. (12) is the Mayer function which, according to Eq. (21), corresponds to the sum of non-zero contributions of the saddle-point interaction (9) and the kinetic interaction (15):

\[
f_{\Delta}^{\mu} = \exp \left[ \beta (2u_{\Delta}^{\mu} - \Delta_{\mu}^{\mu}) \right] - 1, \quad f_{\nu}^{\mu} = \exp \left( \beta u_{\nu}^{\mu} \right) - 1 \quad (44)
\]

where \( u_{\nu}^{\mu} \) is the nearest-neighbor kinetic interaction.

The vacancy correlation effects in concentrated alloys will be described using two different approximations:

(i) The simplest "Lidiard-Le Claire" approximation which supposes that a vacancy that leaves the first neighbor shell of a solute atom does not return \( [8] \). It corresponds to the nearest-neighbor effective interaction:

\[
h_{n} = \delta_{n,1} h_{1} \quad (11)
\]

and will be called the "nearest-neighbor-jump approximation" (NNJA). For the NNJA, Eqs. (33)-(36) include only terms with \( n = 1 \) and \( m = 1 \), and Eqs. (34) and (37) take the form:

\[
l_{p,1}^{\lambda} = \sum_{k=1}^{4} (\hat{w}_{01}^{p}(n_{k} - n_{k+4} - n_{1,k} + n_{1,k+4})), \quad (45)
\]

\[
m_{p,\Delta}^{q} = \sum_{k=1}^{4} (\hat{w}_{0k}^{p} - \hat{w}_{0,k+4}^{p}) n_{1,k}^{q} \quad (46)
\]

\[
t_{p,1}^{q \lambda} = \sum_{k=1}^{4} (\hat{w}_{0k}^{p} n_{1,k}^{q} \sum_{l=1}^{4} (n_{i} - n_{i+4} - n_{k,l} + n_{k,l+4}^{\lambda})). \quad (47)
\]

(ii) The more refined approximation suggested by Bocquet \( [3] \) which neglects the probability of return of a vacancy which leaves the second shell of neighbors, to be called "the second-shell-jump" approximation (SSJA). It describes the vacancy correlation effects with the accuracy of the order of percents \( [3] \) sufficient for the most of applications. In Eqs. (33)-(36), SSJA corresponds to \( n_{\text{max}} = 5 \), that is, to the presence of five fields \( h_{n} \) with the following vectors \( R_{n,1} \) in Eq. (36) (in \( 0/2 \) units):

\[
R_{1,1} = (0, 1, 1), \quad R_{2,1} = (0, 0, 2), \quad R_{3,1} = (1, 2, 1), \quad R_{4,1} = (1, 1, 2) \quad \text{and} \quad R_{5,1} = (0, 0, 2) \quad (48)
\]

while the set \( I_{n}^{p} \) of vectors \( R_{n,1} \) in Eqs. (44) and (47) for \( n \) equal to \( 1, 2, 3, 4 \) and \( 5 \) includes 6, 1, 8, 4 and 4 vectors \( R_{n,1}^{p} \), respectively.

Therefore, to find atomic fluxes \( J_{p,n}^{\lambda} \) in Eqs. (33) we should calculate statistical averages of three different types: quantities \( \bar{w}_{p}^{\lambda} = \langle \hat{w}_{01}^{p} \rangle \) in Eq. (12); quantities \( l_{p,1}^{\lambda} \) and \( m_{p,\Delta}^{q} \) in Eqs. (34) and (37) which include "one-site" averages \( \langle \hat{w}_{01}^{p} \rangle n_{1}^{\lambda} \); and quantities \( t_{p,1}^{q \lambda} \) in Eq. (37) which include "two-site" averages \( \langle \hat{w}_{01}^{p} n_{1}^{q} n_{1}^{\lambda} \rangle .

IV. CALCULATIONS OF STATISTICAL AVERAGES

A. Exact relations

Before to discuss methods of calculations of averages \( \bar{w}_{p}, l_{p,n}^{\lambda}, m_{p,\Delta}^{q} \) and \( t_{p,1}^{q \lambda} \) in Eqs. (33)-(37) we consider some exact relations which follow either from definitions of these averages or from the crystal symmetry.

First, we note that according to definitions (27), (34), (37), each such average is proportional to the factor \( \exp (\beta \lambda_{n}) \), that is, to the reduced thermodynamic activity coefficient \( a_{n} \) for vacancies defined by Eqs. (60)-(61) below. This factor enters into the coefficient \( \Gamma_{p} \) in Eqs. (28) and (29) and is determined by the vacancy-solute interactions \( u_{\alpha} \). Therefore, at nonzero solute concentrations \( c_{\alpha} \) these \( u_{\alpha} \) affect all diffusion coefficients, contrary to the commonly accepted ideas \( [2, 3, 11] \).

Second, we note two operator identities which are useful for calculations of one-site or two-site averages, i.e. quantities \( l_{p,n}^{\lambda}, m_{p,\Delta}^{q} \) or \( t_{p,1}^{q \lambda} \) in Eqs. (33)-(36). These identities include the product of the operator \( n_{1}^{\lambda} \) and one of factors in two last products in Eq. (12):

\[
n_{1}^{\lambda} (1 + \sum_{\lambda} n_{1}^{\lambda} l_{p,\Delta}^{\lambda}) = n_{1}^{q} e_{p,\Delta}^{q}, \quad (48)
\]

\[
n_{1}^{q} (1 + \sum_{\lambda} n_{1}^{\lambda} f_{p,1}^{\lambda}) = n_{1}^{q} e_{p,1}^{q} \quad (49)
\]

where we denote for brevity:

\[
e_{p,\Delta}^{q} = \exp [\beta (2u_{\Delta}^{q} - \Delta_{\Delta}^{q})], \quad e_{p,1}^{q} = \exp (\beta u_{1}^{q}) \quad (50)
\]

Note that when index \( q \) in Eqs. (49) corresponds to a host atom: \( q = h \), the factor \( e_{p,\Delta}^{h} \) or \( e_{p,1}^{h} \) in (49) is unity:

\[
e_{p,\Delta}^{h} = e_{p,1}^{h} = 1 \quad (51)
\]

as the product \( n_{1}^{h} n_{1}^{\lambda} \) in (49) is zero. Eqs. (49) imply, for example, that in Eq. (15) for \( l_{p,1}^{h} \) the product \( (1 + \sum_{\lambda} n_{1}^{\lambda} f_{p,\Delta}^{\lambda}) n_{1}^{h} \) in the operator \( \hat{w}_{01}^{p} n_{1}^{h} \) is reduced to \( c_{p,\Delta}^{h} n_{1}^{h} \), while the product \( (1 + \sum_{\lambda} n_{1}^{\lambda} f_{p,1}^{\lambda}) n_{1}^{h} \) is reduced to \( c_{p,1}^{h} n_{1}^{h} \). It simplifies calculations of averages.

Third, we consider the crystal symmetry relations for one-site and two-site averages, denoted as \( v_{p,ij}^{q} \) and \( v_{p,ij}^{q,\lambda} \):

\[
v_{p,ij}^{q} = \langle \hat{w}_{01}^{p} n_{1}^{q} n_{1}^{i} \rangle, \quad v_{p,ij}^{q,\lambda} = \langle \hat{w}_{01}^{p} n_{1}^{q} n_{1}^{i} \rangle. \quad (52)
\]

These relations can be conveniently discussed using Figs. 1 and 2 which illustrate the crystal symmetry of different

FIG. 1: Bond (0,1) in the FCC lattice and its nearest neighbors, sites \( k \) and \( k \) discussed in the text.

FIG. 2: (color online) Schematic representation of bonds of the type \((h, h), (h, \Delta), (\Delta, \Delta), (\Delta, u)\) and \((u, u)\) described in the text. Seven bonds \((0, k)\) and seven bonds \((1, k)\) which belong to the type \((h, u)\) are not shown for clarity of figure.

\[
\]
sites near the (0,1) bond for an inter-site jump $p = v$. These sites can be divided into three groups: (i) sites 0 and 1, to be called “sites $\Delta$” as occupation of these sites is described in Eq. (12) by the operators $n^\Delta_0$ and $n^\Delta_1$; (ii) sites 2, 4, 9 and 12 being the nearest neighbors of both sites 0 and site 1, to be called “sites $\Delta$” as the occupation operator $n^\Delta_{01}$ or $n^\Delta_{02}$ for these sites enters into Eq. (12) with the factor $f^\Delta_u$ or $f^\Delta_v$. The sites $u$ can also be divided into three groups of the different topology illustrated by Fig. 2: (i) the “vertex” sites 3, 5, 6, 7, 8, 10, 11, and 1; 2, 3, 4, 5, 9, 12, to be called “sides $s$” and (ii) the “central” sites 7 and 1; to be called “sides $c$”. Different types of this site symmetry will be denoted by symbol $\xi$ which takes values $\Delta$ or $u$ or, for a more detailed description, $\Delta$, $v$, $s$, and $c$.

TABLE I. Changes of positions of lattice sites under rotation of the FCC lattice that transforms bond (0, $k$) into bond (0,1).

| $k$ | Components of vector $\mathbf{R}$ | Position of sites |
|-----|----------------------------------|-------------------|
| 1   | $(x, y, z)$                      | 1 2 3 4 5 6 7 8 9 10 11 12 |
| 2   | $(-y, x, z)$                     | 4 1 2 3 5 6 7 12 9 10 11 |
| 3   | $(y, -y, z)$                     | 3 4 1 2 7 8 5 6 11 12 9 10 |
| 4   | $(x, -z, y)$                     | 2 3 4 1 6 7 8 5 10 11 12 9 |
| 5   | $(y, -z, -x)$                    | 10 7 11 1 9 5 12 2 6 8 4 |
| 6   | $(-y, -z, x)$                    | 11 3 10 7 12 1 9 5 4 2 6 8 |
| 7   | $(x, -y, -z)$                    | 7 6 5 8 3 2 1 4 10 9 12 11 |
| 8   | $(y, -z, -x)$                    | 10 7 11 3 9 5 12 1 6 8 4 2 |
| 9   | $(-z, y, x)$                     | 12 4 11 8 9 2 10 6 1 3 7 5 |
| 10  | $(-z, -x, y)$                    | 8 12 4 11 6 9 2 10 5 1 3 7 |
| 11  | $(z, -x, -y)$                    | 6 10 2 9 8 11 4 12 7 3 1 5 |
| 12  | $(z, y, -x)$                     | 9 6 10 2 12 8 11 4 5 7 3 1 |

The above-discussed symmetry relations can be used to simplify Eq. (15) for $t^\lambda_{p,1}$ which is originally written as

$$t^\lambda_{p,1} = \langle w^p_{01}[(n_1 + n_2 + n_3 + n_4 - n_5 - n_6 - n_7 - n_8)^\lambda 
- (n_1 + n_2 + n_3 + n_4 - n_5 - n_6 - n_7 - n_8)^\lambda] \rangle. \quad (53)$$

First, three last terms in the second brackets can be rewritten according to Eq. (45). Second, terms with $n_0^\lambda$ and $n_1^\lambda$ in (53) vanish as the operator $w^p_{01}$ (12) includes factors $n_0^\lambda$ and $n_1^\lambda$ while $n_0^\lambda n_1^\lambda = 0$. Thus we obtain:

$$t^\lambda_{p,1} = \langle w^p_{01}[(n_2 + n_4 + n_9 + n_{12})^\lambda + (n_3 - n_5 
- n_3 + n_5 - n_8 - n_8 - n_2 - n_4) - n_7 - n_1)^\lambda] \rangle. \quad (54)$$

Figs. 1 and 2 show that four $\Delta$-sites, 2, 4, 9, 12, as well as four $v$-sites, 3, 5, 6, 7, eight $s$-sites, 8, 10, 11, 2, 4, 9, 12, and two $c$-sites, 7 and 1, are equivalent to each other. Therefore, Eq. (54) includes only three different terms:

$$t^\lambda_{p,1} = (4\nu^\Delta_{p} - 4\nu^s_{p} - 2u^\lambda_{p}). \quad (55)$$

where $\nu^\lambda_{p}$ means the one-site average $\nu^\lambda_{ps}$ (52) for a site $i$ of the symmetry $\xi$:

$$\nu^\lambda_{p\Delta} = \langle w^p_{01}n^\lambda_2 \rangle, \quad \nu^\lambda_{ps} = \langle w^p_{01}n^\lambda_6 \rangle, \quad \nu^\lambda_{pc} = \langle w^p_{01}n^\lambda_7 \rangle. \quad (56)$$

Expressions (40) and (42) for $m^q_{p,1}$ and $t^q_{p,1}$ include operators $w^q_{0i}$ which describe atomic jumps along bonds (0, $k$) rather than along the bond (0,1) considered above. To use the above-discussed symmetry relations, we can employ the rotation of the FCC lattice which transforms bond (0, $k$) into (0,1) one. Table I shows changes of the positions of different sites under such rotations. Using Table I we can write $m^q_{p,1}$ in (40) as

$$m^q_{p,1} = \langle w^p_{01}(n_4 + n_9 + n_8 - n_3 - n_11 - n_7 - n_10)^q \rangle 
= (2u^q_{p\Delta} - 2u^q_{ps} - u^q_{pc}). \quad (57)$$

It implies:

$$t^q_{p,1} = 2m^q_{p,1} \quad (58)$$

where we use the same considerations and notation as in Eqs. (53), (56), while index $q$ corresponds to either a solute atom $\lambda$ or a host atom $h$.

The similar methods can be used to explicitly write the average $t^q_{p,1}$ in (17). It can be written as the sum of two terms, the “one-site” and the “two-site” one:

$$t^q_{p,1} = t^q_{1p} + t^q_{2p}. \quad (59)$$

The one-site term $t^q_{1p}$ has the form similar to (50):

$$t^q_{1p} = \delta_{p\lambda} \left(2u^q_{p\Delta} + 2u^q_{ps} + 4u^q_{ps} + u^q_{pc} \right) \quad (60)$$

where $\nu^\lambda_{pv}$ is defined similarly to other $\nu^\lambda_{ps}$ in (55):

$$\nu^\lambda_{pv} = \langle w^p_{0i}n^\lambda_j \rangle. \quad (61)$$

The two-site term $t^q_{2p}$ in (59) includes 21 non-equivalent averages $\nu^\lambda_{pj}$, which can be grouped into terms $t^q_{p,jj'}$ corresponding to symmetries $\xi$ and $\xi'$ of sites $i$ and $j$:

$$t^q_{2p} = \sum_{\xi,\xi'} t^q_{p,\xi\xi'}. \quad (62)$$
where both $\xi$ and $\xi'$ takes the value $\Delta$, $v$, $s$ or $c$. The non-zero terms $t^q_{p,\xi} A$ in (62) can be written as follows:

$$
t^q_{p,\Delta} = (4\nu_{2,4} + 2\nu_{2,9} A),
$$

$$
t^q_{p,\Delta s} = -2(\nu_{2,9} A + \nu_{2,10} + \nu_{2,11}),
$$

$$
t^q_{p,\Delta c} = -4(\nu_{2,7} A),
$$

$$
t^q_{p,\Delta \xi} = 2(\nu_{3,10} - \nu_{3,6} + \nu_{3,3}),
$$

$$
t^q_{p,v} = 2(\nu_{3,5} - \nu_{3,3}),
$$

$$
t^q_{p,\xi c} = 2(\nu_{3,7} + \nu_{6,1} A),
$$

$$
t^q_{p,v \xi} = (\nu_{1,1} A).$$

Here the upper index $p$ at averages $\langle \xi \rangle$ with $\xi \neq \xi'$ not presented in Eqs. (63), $\gamma$ can be obtained from those given in (63) by interchanging indices $q$ and $\lambda$.

The above-discussed relations of symmetry can also be used to calculate quantities $\lambda^q_{n,\gamma}$, $m^q_{p,v}$, and $t^q_{p,\xi}$ in Eqs. (34)-(37) used in the SSJA. This is illustrated below.

### B. Kinetic mean-field calculations

In this section we describe calculations of averages $\langle \omega_{q,\xi} \rangle$, $b^q_{p,v}$, and $t^q_{p,\xi}$ in Eqs. (42), (34), (37) using the simplest approximation which neglects fluctuations of occupation numbers $n^q_i$: each $n^q_i$ is replaced by its mean value $\langle n^q_i \rangle = c_p$. At the same time, thermodynamic quantities, in particular, chemical potentials $\lambda_p$ in Eqs. (26), will be found using the more exact, pair-cluster approximation – PCA (or “cluster variation method for pair clusters” (21)). It can significantly raise the accuracy of calculations with respect to the usual mean-field approximation (MFA), particularly for dilute alloys (21 22). To differ this approach from the usual MFA, we call it “the kinetic mean-field approximation” (KMFA).

Let us first find the KMFA expression for the average $\langle \omega_{q,\xi} \rangle$ of the operator $\omega_{q,\xi}$ given by Eq. (42). Replacing each $n^q_i$ in (42) by the site fraction $c_p$, we obtain:

$$\langle \omega_{q,\xi} \rangle_{\text{KMFA}} = \langle \omega_{q,\xi} \rangle = \Gamma_p c_p S^q_{p,\Delta} S^q_{s,\Delta}. \tag{64}$$

The upper index "0" at averages $\omega_p$, $\nu_p$, $m_p$, $l_p$ and $t_p$ will mean “KMFA”, and we denote for brevity:

$$S_{p,\Delta} = \left(1 + \sum_{\alpha} \lambda_{p,\alpha} f_{p,\Delta}^{\alpha}\right), \quad S_u = \left(1 + \sum_{\mu} c_{p,\mu} f_{p,\mu}^{\alpha}\right). \tag{65}$$

The factor $\Gamma_p$ in (64) according to (29), can be expressed via the activation frequency $\nu_p$ and the chemical potentials $\lambda_p$ of vacancies or solute atoms with respect to host atoms. Each $\lambda_p$ is the sum of the ideal solution term $\lambda^o_p = T \ln(c_p/c_h)$ and the interaction term $\lambda^i_p$:

$$\lambda^o_p = \ln(c_p/c_h) + \beta \lambda^o_p
$$

$$\lambda^o_p = \ln(c_p/c_h) + \beta \lambda^o_p \tag{66}$$

In a dilute alloy, the interaction term $\lambda^i_p$ is linear in the solute site fractions $c_s$. We will describe this term by the PCA expression which for dilute alloys becomes exact (22). For a binary alloy, these expressions are given below by Eqs. (77), while for a multi-component dilute alloy they can be obtained from Eqs. (26)-(31) in (22):

$$\beta \lambda^{n,\gamma} = - \sum_{\gamma=1}^{n} z_n f_{\gamma}^{\gamma} c_\gamma \tag{67}$$

$$\beta \lambda^{n,\gamma} = - \sum_{\gamma=1}^{n} z_n f_{\gamma}^{\gamma} c_\gamma. \tag{67}$$

Here $z_n$ is the coordination number for the $n$-th shell in the crystal, and $f^{\gamma}$ is the Mayer function for the configurational interaction $v^{\gamma}_{\gamma}$ in this shell:

$$f^{\gamma}_{n} = \exp (\beta v^{\gamma}_{n} - 1). \tag{68}$$

Using Eqs. (29) and (30), we can write $w^{0}_{p}$ in (41) as

$$w^{0}_{p} = c_p \omega_{p} \tag{69}$$

where the quantity $\omega_{p}$ is defined as follows:

$$\omega_{n} = \gamma_{n} c_{a} a_{n} a_{n} S^4_{\Delta} S^4_{s,\Delta} \tag{70}$$

$$\omega_{h} = \gamma_{h} c_{a} a_{h} c_{h} S^4_{\Delta} S^4_{s,\Delta}. \tag{70}$$

Here the factor $a_{v}$ or $a_{a}$ defined by the relation

$$a_v = \exp(\beta \lambda^{v,\gamma} \int), \quad a_a = \exp(\beta \lambda^{a,\gamma} \int) \tag{71}$$

can be called “the reduced activity coefficient” for a vacancy or for a solute atom (our $a_a$ is related to the activity coefficient $\gamma_{a}$ used, e. g., in [8] as: $a_a = c_h \gamma_{a}$).

When $c_{a} \rightarrow 0$, factors $a_{v}, a_{a}, S_{p,\alpha}, S_{u}$ in (65) and (71) tend to unity, thus quantities $\omega_{p}$ in (70) take the values

$$\omega^{0}_{a} = c_{a} \gamma_{a}, \quad \omega^{0}_{h} = c_{a} \gamma_{h}. \tag{72}$$

Hence $\omega^{0}_{p}$ has the meaning of the mean frequency of the vacancy-(p-species atom) exchanges in a dilute alloy. For a concentrated alloy, $\omega_{p}$ can be viewed as the average value of this frequency found in the KMFA. Note that the mean frequency $\omega^{0}_{a}$ differs from the “solute jump frequency" $\omega_{a}$ used in the standard five-frequency model [1 8] which is related to $\omega^{0}_{a}$ as follows:

$$w_{a} = \omega^{0}_{a} e^{c_{a}}, \quad e^{c_{a}} = \exp(\beta v^{0}_{1}) \tag{73}$$

where $v^{0}_{1}$ is the nearest-neighbor vacancy-solute interaction. Factor $e^{c_{a}}$ in (73) corresponds to the factor $\exp(\beta E_{A,1})$ in (7), and it is canceled in the mean frequency $\omega^{0}_{p}$ due to the statistical averaging in Eqs. (65).

Discussing calculations of one-site averages $v^{0}_{p}$ in Eqs. (55), (58) and (60) we first note that the differences between averages which include operators of occupation of sites of the symmetry $v$, $s$ or $c$ mentioned above arise only due to the inter-site correlations. Hence these differences are not manifested in the KMFA. Therefore, each of indices $v$, $s$, $c$ in Eqs. (59)- (61) can be replaced by the
common index $u$. Second, using identities (49) we see that the average $\nu_{\beta}^\theta = \langle \nu_{\beta}^\theta \rangle$ differs from the average $\langle \nu_{\beta}^\theta \rangle = w_{\beta}^0$ by replacing one of factors $S_{\beta\gamma}$ in Eq. (64) (with $S_{\beta u} \equiv S_u$) by the appropriate factor $c_{\beta}c_{\gamma}q$ with $c_{\beta}q$ from Eqs. (50). It yields the following relations:

$$
\nu_{\beta\Delta}^\theta = c_{\beta}c_{\gamma}q_{\beta}^\Delta, \quad \nu_{\beta}^\Delta = c_{\beta}c_{\gamma}q_{\beta}^\Delta
$$

(74)

where we denote for brevity:

$$
\eta_{\beta}^\theta = \eta_{\beta}^\Delta, \quad \eta_{\beta} = \eta_{\beta}^\Delta/ \eta_{\beta}^\Delta.
$$

(75)

The same methods can be used for the KMFA calculations of two-site averages $\nu_{\beta,ij}^\theta$ in (63). Hence the KMFA expressions for one-site and two-site averages are similar:

$$
\nu_{\beta_i}^\theta = c_{\beta}c_{\gamma}q_{\beta_i}^\theta, \quad \nu_{\beta,ij}^\theta = c_{\beta}c_{\gamma}c_{\lambda}q_{\beta\lambda}^\theta \eta_{\gamma}^\theta\xi_{\gamma}^\lambda.
$$

(76)

Here indices $\xi$ and $\eta_i$ equal to $\Delta$ or $u$ indicate the above-mentioned symmetry of site $i$ and site $j$, respectively, and relations $\eta_{\beta\gamma}^\theta = \eta_{\beta\gamma}^\Delta$, $\eta_{\beta\gamma} = \eta_{\beta\gamma}^\Delta/ \eta_{\beta\gamma}^\Delta$ are implied.

The resulting KMFA expressions for quantities $m_{\beta,1}^q$,

$t_{\beta,1}^q, \quad t_{\beta,2}^q, \quad t_{\beta,2}^q$ and $t_{\beta,2}^q$ in Eqs. (58) and (59) can be written as follows:

$$
m_{\beta,1}^q = c_{\beta}c_{\gamma}q_{\beta}^1(2\eta_{\beta}^\theta - 3\eta_{\beta}^\theta),
$$

$$
t_{\beta,1}^q = \delta_{\xi\eta}c_{\beta}c_{\gamma}q_{\beta}^1(2\eta_{\beta}^\theta + 7\eta_{\beta}^\theta),
$$

$$
t_{\beta,2}^q = c_{\beta}c_{\gamma}c_{\lambda}q_{\beta\lambda}^\theta \left[ 6\eta_{\gamma}^\theta\eta_{\lambda}^\theta \right]
$$

$$
-12(\eta_{\beta\Delta}^\theta\eta_{\Delta}^\theta + \eta_{\beta\Delta}^\theta\eta_{\lambda}^\theta) + 11\eta_{\beta\lambda}^\theta\eta_{\lambda}^\theta].
$$

(77)

Calculations of averages $t_{\beta,1}^q, t_{\beta,2}^q, m_{\beta,1}^q$ and $t_{\beta,2}^q$ in Eqs. (34), (37) for values $n, m > 1$ corresponding to the SSJA can be made similarly to those for the NNJA described above, though description of rotations of vectors $R_{\beta+}$ and $R_{\beta-}$ in (37) (analogous to that given in Table I for vectors $R_{1k}$) should be made for each $n$ and $m$ separately. The results can be written in terms of “reduced” quantities $t_{\beta,1}^q, m_{\beta,1}^q, m_{\beta,2}^q$ defined by the relations:

$$
t_{\beta,1}^q = c_{\beta}c_{\gamma}q_{\beta}^1, \quad m_{\beta,1}^q = c_{\beta}c_{\gamma}q_{\beta}^\theta m_{\beta,1}^q
$$

(78)

where $\omega_{\beta}$ is the same as in Eqs. (70). Expressions for quantities $t_{\beta,2}^q, m_{\beta,2}^q, m_{\beta,2}^q, m_{\beta,2}^q$ in (78) via $\eta_{\beta}^\theta$ and $\eta_{\beta}^\theta$ in (70) and the factor

$$
\xi_{\beta}^\theta = (\eta_{\beta}^\theta - 1)
$$

(79)

are given in Table II.

TABLE II. Reduced values $t_{\beta,1}^q, m_{\beta,1}^q, m_{\beta,1}^q, m_{\beta,1}^q$

| $n$ | 1 | 2 | 3 | 4 | 5 |
|-----|---|---|---|---|---|
| $t_{\beta,1}^q$ | $(4\eta_{\beta}^\Delta - 6\eta_{\beta}^\lambda)$ | $2\xi_{\beta}^\lambda$ | $4\xi_{\beta}^\lambda$ | $4\xi_{\beta}^\lambda$ | $2\xi_{\beta}^\lambda$
| $t_{\beta,2}^q$ | $(2\eta_{\beta}^\Delta - 3\eta_{\beta}^\lambda)$ | $4\xi_{\beta}^\lambda$ | $\xi_{\beta}^\lambda$ | $2\xi_{\beta}^\lambda$ | $\xi_{\beta}^\lambda$

Similarly, matrices $t_{\beta,1}^q$, which enter into Eqs. (37) can be expressed via the “reduced” matrices $t_{\beta,1}^q, \quad t_{\beta,1}^q, \quad t_{\beta,1}^q, \quad t_{\beta,1}^q$:

$$
t_{\beta,1}^q = c_{\beta}c_{\gamma}q_{\beta}^\theta (\delta_{\xi\eta}t_{\beta,1}^q + c_{\lambda}t_{\beta,1}^q).
$$

(80)

Here the matrix $t_{\beta,1}^q$ has a relatively simple form:

$$
\begin{pmatrix}
2\eta_{\beta}^\Delta + 7\eta_{\beta}^\lambda - 4\eta_{\beta}^\lambda - 2\eta_{\beta}^\lambda - \eta_{\beta}^\lambda

-4\eta_{\beta}^\lambda

4\eta_{\beta}^\lambda + 8

0

-4\eta_{\beta}^\lambda

-4\eta_{\beta}^\lambda

0

2\eta_{\beta}^\lambda + 9

-1

-1

-2\eta_{\beta}^\lambda

-1

-2

2\eta_{\beta}^\lambda + 10

-2

-\eta_{\beta}^\lambda

0

-2

-2

\eta_{\beta}^\lambda + 11

\end{pmatrix}
$$

while the matrix $t_{\beta,2}^q$ can be written as follows:

$$
\begin{pmatrix}
7\eta_{\beta}^\lambda - 4\eta_{\beta}^\lambda - 2\eta_{\beta}^\lambda - \eta_{\beta}^\lambda

4\eta_{\beta}^\lambda

\eta_{\beta}^\lambda + 1

4\eta_{\beta}^\lambda

4\eta_{\beta}^\lambda

\eta_{\beta}^\lambda + 2

\eta_{\beta}^\lambda

\eta_{\beta}^\lambda

\eta_{\beta}^\lambda

\eta_{\beta}^\lambda

\end{pmatrix}
$$

where the diagonal elements $t_{\beta,2}^q$ are:

$$
\begin{pmatrix}
\delta_{\xi\eta}t_{\beta,1}^q + c_{\lambda}t_{\beta,1}^q

\delta_{\xi\eta}t_{\beta,1}^q + c_{\lambda}t_{\beta,1}^q

\delta_{\xi\eta}t_{\beta,1}^q + c_{\lambda}t_{\beta,1}^q

\delta_{\xi\eta}t_{\beta,1}^q + c_{\lambda}t_{\beta,1}^q

\delta_{\xi\eta}t_{\beta,1}^q + c_{\lambda}t_{\beta,1}^q

\delta_{\xi\eta}t_{\beta,1}^q + c_{\lambda}t_{\beta,1}^q

\delta_{\xi\eta}t_{\beta,1}^q + c_{\lambda}t_{\beta,1}^q

\delta_{\xi\eta}t_{\beta,1}^q + c_{\lambda}t_{\beta,1}^q

\delta_{\xi\eta}t_{\beta,1}^q + c_{\lambda}t_{\beta,1}^q

\delta_{\xi\eta}t_{\beta,1}^q + c_{\lambda}t_{\beta,1}^q

\end{pmatrix}
$$

(81)

while non-diagonal elements are expressed via only two quantities $\chi_{\beta}^q$ and $\xi_{\beta}^q$:

$$
\begin{pmatrix}
(4\eta_{\beta}^\lambda - 5\eta_{\beta}^\lambda - 4\eta_{\beta}^\lambda + 6\eta_{\beta}^\lambda)

\chi_{\beta}^q

\chi_{\beta}^q

\chi_{\beta}^q

\chi_{\beta}^q

\chi_{\beta}^q

\chi_{\beta}^q

\chi_{\beta}^q

\chi_{\beta}^q

\chi_{\beta}^q

\end{pmatrix}
$$

(82)

The KMFA calculations described above neglect contributions of fluctuations of occupation numbers $n_{\beta}^q$ in the statistical averages. Calculations of such contributions can be made using the more refined statistical methods, such as the pair-cluster approximation - PCA [20], and they will be described elsewhere together with their contribution to the enhancement of chemical diffusion.

At the same time, these calculations show that these fluctuative contributions are typically not very significant, and the above-described KMFA expressions are usually sufficient for the realistic description of diffusion, particularly in dilute alloys.
V. DIFFUSION IN BINARY ALLOYS

A. General expressions for Onsager coefficients in a binary alloy

For a binary alloy $AB$ with $h = A$ and $\alpha = B$, fields $h^\alpha_{max}$ in Eqs. (85) and (86) are zero due to the antisymmetry property (23), thus Eqs. (86) take the form of a system of $n_{max}$ equations for $n_{max}$ fields $h^\alpha_{max} = h^B_{max}$:

$$\sum_{m=1}^{n_{max}} a_{m}h^B_{m} = (m^A_{m} \alpha) \delta \mu_{Be} - (m^B_{m} \alpha) \delta \mu_{Ar},$$

$$a_{nm} = (t^B_{h,n} - t^A_{B,n} - 2m^B_{h,n} \delta m_1)$$  \hfill (83)

where $\delta m_1$ is unity when $m = 1$ and zero otherwise.

In the NNJA, Eqs. (83) include only one field $h^q_{max}$ which is simply expressed via $m^q_{p,1}$ and $\delta p_{11}$ in (57), (59):

$$h^B_{1} = (m^A_{1} \alpha) \delta \mu_{Be} - (m^B_{1} \alpha) \delta \mu_{Ar})/a_{11},$$

$$a_{11} = (t^B_{1,1} - t^A_{B,1} - 2m^B_{2,1} \delta m_1)$$  \hfill (84)

Substituting this $h^B_{max}$ in Eq. (83) with $n_{max} = 1$ and using also Eq. (86), we obtain the following relations between fluxes $J^p_{0 \rightarrow 1}$ and differences $\delta p_{11}$:

$$J^B_{0 \rightarrow 1} = -\beta \delta \mu_{Be} \left[ w_{B} + 2m^A_{1} \alpha (\bar{w}_{B} + m^B_{1} \alpha) / a_{11} \right]$$

$$+ \beta \delta \mu_{Ar} 2m^B_{1} \alpha (\bar{w}_{B} + m^B_{1} \alpha) / a_{11}$$

$$J^A_{0 \rightarrow 1} = -\beta \delta \mu_{Be} 2m^A_{1} \alpha (\bar{w}_{B} + m^B_{1} \alpha) / a_{11}$$

$$- \beta \delta \mu_{Ar} [w_{A} - 2(m^B_{1} \alpha)^2 / a_{11}]$$  \hfill (85)

which determine the Onsager coefficients $L_{pq}$ in (11).

Note that the Onsager symmetry relation,

$$L_{BA} = L_{AB},$$

in our approach is obeyed identically. According to Eq. (55), Eq. (86) implies:

$$m^B_{1,1} + m^A_{2,1} = -w_{B}.$$  \hfill (87)

Using Eqs. (55)-(58) we can re-write (87) as

$$\langle \hat{w}_{B} (2n_{B} + n^A_{4}) - 2(n_{A}^B + n_{5}^B) \rangle = -\langle \hat{w}_{B} \rangle, \hfill (88)$$

which holds identically as $(n_{B}^B + n^A_{4}) \equiv 1$.

One can show that the symmetry relation (86) holds also for the SSJA. Presence of this relation irrespective of site fractions and approximations used illustrates the theoretical consistency of the master equation approach.

Using Eqs. (55) and (86), we can write the general NNJA expressions for Onsager coefficients $L_{pq}$ as follows:

$$(T/\eta_{B})_{LBB} = \left[\frac{n^0_{B}}{2} - 2(m^B_{1,1})^2 / a_{11} \right],$$

$$(T/\eta_{B})_{LAB} = L_{BA} = \left(2m^A_{1,1} m^B_{2,1} / a_{11} \right),$$

$$(T/\eta_{B})_{LAA} = \left[\frac{n^0_{A}}{2} - 2(m^B_{1,1})^2 / a_{11} \right].$$  \hfill (89)

To write explicit expressions for $L_{pq}$ in (89), it is convenient to omit index $\alpha = B$ of the only kind of solute atoms in the site fraction $c_B$ and in quantities $\eta^B_{\alpha b}, c^B_{\alpha b}, \eta^A_{\alpha b}$ and $c^A_{\alpha b}$ defined by Eqs. (70) and (78), and also to employ the "reduced" denominator $D_{nn}$ rather than the quantity $a_{11}$ from (54), as well as the frequency ratio $z = \omega_B / \omega_A$ rather than the frequency $\omega_B$ from (71):

$$c_B = c, \quad \eta^B_{\alpha A} = \eta_{AA}, \quad c^B_{\alpha A} = c_{AA},$$

$$\eta^A_{\alpha B} = \eta_{B}, \quad c^A_{\alpha B} = c_{B}, \quad a_{11} = cc_{BA}\omega_{D_{nn}},$$

$$z = \omega_B / \omega_A = \gamma_{BB} \omega_{B} S^4_{\Delta} / \gamma_{AA} S^4_{\Delta}.$$  \hfill (90)

Using KMFA expressions (70), (78), (80) for quantities $u^\alpha_{\nu}, m^\alpha_{n1}, m^\alpha_{n1}$ and $\delta^\alpha_{\nu_{11}}$ in (54) and (59), we can write the NNJA expressions for Onsager coefficients as follows:

$$(T/\eta_{A})_{LAA} = \omega_{ACA} \left[1 - 2c(3\eta_{n} - 2\eta_{AA})^2 / D_{nn} \right],$$

$$(T/\eta_{B})_{LAB} = \omega_{BC} 2(3\eta_{n} - 2\eta_{AA}) \times (3\eta_{n} - 2\eta_{BB}) / D_{nn},$$

$$(T/\eta_{B})_{LBB} = \omega_{BC} \left[1 - 2c_{AA} \right] \times (3\eta_{n} - 2\eta_{BB})^2 / D_{nn}.$$  \hfill (91)

The denominator $D_{nn}$ in (91) can be conveniently written as the sum of two terms, that without the common factor of site fraction $c$ and that which includes this factor:

$$D_{nn} = (d_{11,1} + c d_{21,1}). \hfill (92)$$

Here quantities $d_{11,1}$ and $d_{21,1}$ are expressed via the reduced parameters $\nu^\alpha_{\nu_{11}}, t^\alpha_{\nu_{11}}$, and $\delta^\alpha_{\nu_{11}}$ in (78) and (80) in accordance with Eqs. (54) and (49):

$$d_{11,1} = (d^B_{1,1,1} - 2
u^B_{1,1}),$$

$$d_{21,1} = (d^B_{2,1,1} - z \delta^B_{2,1}) \hfill (93)$$

or, explicitly:

$$d_{11,1} = (2\eta_{AA} + 7\eta_{n}) + 2z(3\eta_{n} - 2\eta_{BB}),$$

$$d_{21,1} = \left(6\eta^4_{AA} - 24\eta_{AA}\eta_{n} + 11\eta_{n}^2 \right) \times \left[ \frac{\eta_{BB} \omega_{D_{nn}} - 12(\eta_{BB} \omega_{n} + \eta_{BB} \omega_{n}^4) + 11\eta_{n}^4 \omega_{n} \right]. \hfill (95)$$

In Eqs. (49) and (93), quantities $\eta^A_{\alpha A}, \eta^A_{\alpha} \eta_{\alpha} \eta_{\alpha}$ are defined by Eqs. (70) and (51):

$$\eta^A_{\alpha A} = 1 / S_{B \alpha}, \quad \eta^A_{\alpha} = 1 / S_{u}, \quad \eta_{\alpha} = \eta_{\alpha} S_{B \alpha} / S_{AA},$$

$$\eta_{\alpha} = \epsilon_{u}/ S_{u}, \quad \eta_{BB} = \epsilon_{BB}/ S_{BB},$$

$$S_{AA} = (1 + \epsilon_{AA}), \quad S_{BB} = (1 + \epsilon_{BB}),$$

$$\epsilon_{u} = (1 + \epsilon_{u}), \quad f_{AA} = (\epsilon_{AA} - 1),$$

$$f_{BB} = (\epsilon_{BB} - 1), \quad f_{u} = \epsilon_{u},$$  \hfill (96)

while factors $\epsilon_{AA}$ and $\epsilon_{u}$ in (90) are defined by Eqs. (90), (50), and (44).

Let us also explicitly write the reduced activity coefficients $a_v$ and $a_B$ in (71). Using for chemical potentials...
\( \lambda_a \) and \( \lambda_B \) their PCA expressions given by Eqs. (39) in Ref. [17], we obtain for coefficients \( a_v \) and \( a_B \) in (71):

\[
a_v = \exp \left\{ - \sum_{n=1} z_n \ln [1 + 2c f_n^{Bv} / (R_n + 1)] \right\},
\]

\[
a_B = \exp \left\{ - \sum_{n=1} z_n \ln [1 + 2c f_n^{BB} / (R_n + 1)] \right\}.
\]

(97)

Here \( z_n \), \( f_n^{Bv} \) and \( f_n^{BB} \) are the same as in (67):

\[
f_n^{Bv} = \exp (-\beta v_n^{Bv}) - 1, \quad f_n^{BB} = \exp (-\beta v_n^{BB}) - 1, \quad \text{while} \quad R_n \text{ is expressed via } f_n^{BB} \text{ as follows:}
\]

\[
R_n = (1 + 4cc_A f_n^{BB})^{1/2}.
\]

(99)

For the SSJA, the general expressions for Onsager coefficients in a concentrated binary alloy can be obtained from Eqs. (78)-(81) similarly to the NNJA expressions (91). However, these general expressions are cumbersome. Therefore, these expressions will be given elsewhere in connection with their contributions to the enhancement of chemical diffusion, while in Sec. VC we present them only for the case of a dilute alloy.

**B. Expressions for chemical diffusion coefficients and correlation factors in a concentrated binary alloy**

In this section we present explicit expressions for the chemical (or “intrinsic” [8]) diffusion coefficients \( D_A \) and \( D_B \). First we discuss the thermodynamic “activity factor” \( A_{ac} \) which enters into these expressions. As vacancies for processes under consideration are locally equilibrium and their chemical potential \( \mu_v \) is zero [8], differences \( \mu_{qv} = (\mu_q - \mu_v) \) in Eq. (22) can be replaced by absolute chemical potentials \( \mu_{pq} = \partial F / \partial N_q \) where \( F \) is the total free energy and \( N_q \) is the total number of \( q \)-species atoms. These \( \mu_{pq} \) are related to quantity \( \lambda_a = \lambda_B \) in Eqs. (22) and the grand canonical potential per atom, \( \Omega \), by the following relations [22]:

\[
\mu_A = \Omega, \quad \mu_B = \lambda_B + \Omega \quad \text{(100)}
\]

where the PCA expression for \( \Omega \) is presented in (22):

\[
\Omega = T \ln c_A - \frac{1}{2} T \sum_{n=1} z_n \ln \left[ 1 - 2c f_n^{BB} / (R_n + 1 + 2c f_n^{BB}) \right].
\]

(101)

while \( z_n \) and \( f_n^{BB} \) are the same as in (67). The diffusion coefficients \( D_p \) are defined by the Fick’s first law [8]:

\[
\mathbf{J}_A = -D_A \nabla n_A, \quad \mathbf{J}_B = -D_B \nabla n_B
\]

(102)

where \( \mathbf{J}_p \) is the same as in Eq. (22) and \( n_p \) is the density of \( p \)-species atoms. To write explicit expressions for \( D_p \), we can also use the Gibbs-Duhem relation:

\[
c_A d\mu_A + c_B d\mu_B = c_A d\Omega + c d\mu_B = 0
\]

(103)

which for Eqs. (100), (101) and the PCA expression for \( \lambda_B \) given by Eqs. (60), (71) and (97) can also be checked by a direct calculation. Using Eqs. (22), (102) and (103) and supposing that the mean volume \( \bar{v} \) per atom of an alloy is described by the Vegard’s law:

\[
\bar{v} = \bar{v}_A c_A + \bar{v}_B c_B
\]

(104)

where \( \bar{v}_p \) is the atomic volume of a \( p \)-component in an alloy, we can write \( D_p \) as follows:

\[
D_A = (T/n^2 \bar{v}_A) \left( L_{AA} / c_A - L_{AB} / c \right) A_{ac}, \quad D_B = (T/n^2 \bar{v}_B) \left( L_{BB} / c - L_{AB} / c \right) A_{ac}.
\]

(105)

Here Onsager coefficients \( L_{pq} \) are the same as in (91), while the activity factor \( A_{ac} \) is related to the reduced activity \( a_B \) in Eq. (71) by the following relation:

\[
A_{ac} = 1 + cc_A d \ln a_B / dc = 1 + cc_A d (\beta \lambda_B^{nt}) / dc.
\]

(106)

Substituting \( \beta \lambda_B^{nt} = T \ln a_B \) with \( a_B \) from [97], we obtain:

\[
A_{ac} = 1 - cc_A \sum_{n=1} z_n 2 f_n^{BB} \frac{R_n + 1 - 4c (1 - 2c) f_n^{BB}}{(R_n + 1)(R_n + 1 + 2c f_n^{BB})}.
\]

(107)

Let us now discuss the Onsager coefficients \( L_{pq} \) in (105). Eqs. (91) show that each \( L_{pq} \) can be conveniently expressed via the mean frequency \( \omega_p \) and the reduced “correlative” coefficients \( L_{pq}^{ct} \), which describe vacancy correlation effects and are defined by the following relations:

\[
(T/n^2 \eta_0^A) L_{AA} = \omega_A c_A (1 - c L_{AA}^c), \quad (T/n^2 \eta_0^A) L_{AB} = \omega_B c_A L_{AB}^c, \quad (T/n^2 \eta_0^A) L_{BB} = \omega_B c (1 - c L_{BB}^c).
\]

(108)

Using Eqs. (91), we can concisely write the correlative coefficients \( L_{pq}^c \) in (103) for the NNJA as follows:

\[
L_{AA}^c = 2(3\eta_A - 2\eta_{AA})^2 / D_{nn}, \quad L_{AB}^c = 2(3\eta_A - 2\eta_{AA})(3\eta_A^A - 2\eta_{BB}) / D_{nn}, \quad L_{BB}^c = 2z(3\eta_A^A - 2\eta_{AA})^2 / D_{nn}.
\]

(109)

Eqs. (105) and (109) show that each diffusion coefficient is proportional to several factors of different nature: the mean frequency \( \omega_p \), the correlation factor \( f_p \), and the activity factor \( A_{ac} \), similarly to the dilute alloy case [8]:

\[
D_p = (\alpha_0^2 / n \bar{v}_p) \omega_p f_p A_{ac}, \quad f_A = 1 - (c_A L_{AA}^c + c L_{AA}^c), \quad f_B = 1 - (c_A L_{BB}^c + c L_{BB}^c)
\]

(110)

but factors \( \omega_p \), \( f_p \), \( A_{ac} \) depend on the solute fraction \( c \). Applications of Eqs. (110) to the description of enhancement of chemical diffusion will be described elsewhere.
C. Onsager coefficients in a dilute binary alloy

In the dilute alloy limit $c \to 0$, frequencies $\omega_p$ tend to $\omega_p^0$ in (72), while parameters $z, \eta^A, \eta^\Delta, \eta^u_0$ and $\eta^u$ in (61)-(65), according to (90) and (96), take the following values:

$$z_0 = \gamma_B v / \gamma_A v, \quad (\eta^A_\Delta)_0 = (\eta^u_0)_0 = 1,$$
$$\eta^u_0 = \epsilon_A \Delta, \quad \eta^u = \epsilon_u.$$  

(111)

Here and below, the upper or the lower index “0” at each quantity indicates its value at $c = 0$.

To relate our notation to that commonly used for the five-frequency model [1-9] we note that the jump rates (“frequencies”) $w_n$ of that model in our notation are:

$$w_0 = \omega^A_A, \quad w_1 = \omega^A_A e_\Delta e^B e^B, \quad w_2 = \omega^B e^B e^B,$$
$$w_3 = \omega^A e^B e^B e_u, \quad w_4 = \omega^A e^B$$  

(122)

where $e^B$ is the same as in (73). At the same time, exponential factors $e_u$ and $e_\Delta$ in (122) have a more clear physical meaning than frequencies $w_n$. Eqs. (62)-(66) include also the factor $e_\Delta$ analogous to $e_\Delta A$, which describes influence of a sole atom $B$ near the bond $(ij)$ on the $Bi \rightleftharpoons vj$ jump probability. Thus below we use instead of $w_n$ quantities $x_n$ and $y_n$ defined as follows:

$$x_1 = e_\Delta A, \quad x_2 = \omega^A_B / \omega^A_A, \quad x_3 = \epsilon_u,$$
$$y_1 = e_\Delta = \exp[\beta(2u^A - \Delta^B)]$$  

(113)

with $x_2$ equal to $z_0$ in (111). In this notation, the Mayer functions $f_pA$ and $f_u$ and the low-c values of factors $\xi_u$ and $\xi^A_A$ in Eqs. (96) take the following form:

$$f^A = (x_1 - 1), \quad f^B_A = (y_1 - 1),$$
$$f_u = (x_2 - 1), \quad \xi_u = f_u = (x_4 - 1),$$
$$\xi^A_A(c \ll 1) = -c f_u = -c(x_4 - 1).$$  

(114)

Below we present the low-c expansions for mean frequencies $\omega_p$ and Onsager coefficients $L_{pq}$ up to the first order in $c$, and the zero-order terms for correlative Onsager coefficients $L_{pq}$ and correlation factors $f_pB$ in Eqs. (108)-(110). The fluctuative corrections mentioned in Sec. [IVB] make no contribution to these terms, hence we can use the KMF expressions (109).

Let us first consider the mean frequency $\omega_p$ and define the enhancement factor $b_p^A$ for it by the usual relation:

$$\omega_p(c) = \omega_p^A(1 + c b_p^A).$$  

(115)

Using Eqs. (70) for $\omega_p$ and the PCA expressions (57) for activity factors $a_u$ and $a_B$, we find:

$$b_p^A = (4f_A + 14f_u + b_vB),$$
$$b_p^B = (4f_B + 14f_u + b_vB + b_vB).$$  

(116)

Here $f_pA$ and $f_u$ are the same as in (114), while $b_vB$ and $b_vB$ are contributions of the activity factors, $a_u$ and $a_B$:

$$b_vB = - \sum_{n=1} z_n f_n^B = -12 f_1^B - 6 f_2^B - \ldots$$  

(117)

$$b_vB = - \sum_{n=1} z_n f_n^B = -12 f_1^B - 6 f_2^B - \ldots$$  

(118)

For correlative terms and correlation factors at $c = 0$, $L_{pq}^0$ and $f_p0$, we find from Eqs. (109)-(111) in the NNJA:

$$L_{AA}^0 = 2(3x_4 - x_1)^2 / D_0, \quad L_{AB}^0 = (3x_4 - x_1) / D_0,$$
$$L_{BB}^0 = 2x_2 / D_0, \quad D_0 = (x_2 + 2x_2 + 7x_4).$$  

(119)

$$f_{A0} = 1 - x_2 L_{AB}^0, \quad f_{B0} = 1 - L_{BB}^0.\quad \quad \quad$$  

(120)

In the SSJA, values of $L_{pq}^0$ can be obtained from the general expressions for $L_{pq}$ mentioned in Sec. VIII.

$$L_{AA}^0 = 2 \left[(3x_4 - 2x_2)^2 / D_0 \right] + \rho_D f^2 / D_0^0,$$
$$L_{AB}^0 = 2(3x_4 - 2x_1 - \rho_0 f_u) / D_0^0,$$
$$L_{BB}^0 = 2x_2 / D_0^0, \quad D_0^0 = D_0 - \rho_0 x_4.$$  

(121)

while correlation factors $f_p0$ are expressed via these $L_{pq}^0$ according to Eqs. (120). $D_0$ in (121) is the same as in (111), while $\rho_0$ is related to the “vacancy escape function” $F = F(x_4)$ of the five-frequency model as:

$$\rho_0 = 7(1 - F) = p_N(x_4)/p_D(x_4)$$  

(122)

where $p_N(x)$ and $p_D(x)$ are polynomials found by Bocquet [3]:

$$p_N(x) = (10x^4 + 190x^3 + 1031x^2 + 1594.5x),$$
$$p_D(x) = (2x^4 + 45x^3 + 328x^2 + 930.5x + 855.5).$$  

(123)

For a more accurate description of vacancy correlation effects at low $c$ (used, in particular, in Sec. VIII, the polynomials $P_N$ and $P_D$ in (122) can be taken from Ref. [3].

Using Eqs. (108) and (113), we can write Onsager coefficients at low $c$ as follows:

$$(T/\rho^A_0) L_{AA}^0 = \omega_p^A(1 + c(2\rho^A_0 - 1) - L_{AA}^0)),$$
$$(T/\rho^B_0) L_{AB}^0 = \omega_p^B c L_{AB}^0,$$
$$(T/\rho^A_0) L_{BB}^0 = \omega_p^B c (1 - L_{BB}^0).$$  

(124)

For the case of very low vacancy concentration under consideration: $c_v \ll c_B$, values of $L_{pq}$ in Eqs. (124) with $b_v^A$ and $L_{pq,0}$ given by Eqs. (110)-(111) coincide with those found in the traditional theory [8]. At the same time, the expression for $L_{AA}$ obtained by Nastar [11] corresponds to missing the vacancy-solute interaction term $b_vB$ given by Eq. (116) in the term $b_v^A$ in (124).

VI. ENHANCEMENT OF TRACER SOLVENT DIFFUSION IN A DILUTE BINARY ALLOY

Below we discuss enhancement of diffusion of radioactive isotopes (“tracers”) in a dilute alloy $AB$. The tracer solvent enhancement factor $b_v^A$ was calculated in a number of previous studies reviewed in detail by Nastar [11]. However, some significant contribution to $b_v^A$ discussed

...
below was missed in these studies. The tracer solute enhancement factor $b_{p*}$, to our knowledge, was not calculated, even though experimental values of this factor are known for a number of alloys \[ \text{[10]}. \]

For simplicity, below we use the simplest approximations for both the statistical calculations and the description of vacancy correlation effects employing KMFA and NNJA. Going beyond these approximations, as well as a possible influence of non-pairwise effective interactions $h_{ij}^{\text{eff}}$ in \[ \text{[11]}, \] discussed by Barbe and Nastar \[ \text{[12]} \] for other problems, will be discussed elsewhere in calculations of enhancement factors for chemical diffusion. At the same time, comparison of our results with the available Monte Carlo simulations seems to imply that the effects disregarded in this work make usually a relatively weak influence on the tracer enhancement factors in real alloys.

Therefore, our calculations of both $b_A^*$ and $b_B^*$ use the NNJA equations \[ \text{[9]} \] for fields $h^{\text{eff}}$ and the KMFA expressions \[ \text{[7]} \] for coefficients in these equations.

### A. General equations of diffusion in a ternary alloy

For a ternary alloy which contains components $\alpha$, $\beta$ and $h$, Eqs. \[ \text{[3]} \] take the following form:

\[
\begin{align*}
(m_\alpha^h \delta \mu_\alpha - m_\beta^h \delta \mu_\beta) + h_{\alpha\alpha}(2m_\alpha^h - t_{1h}^\alpha + t_{2h}^\alpha) + h_{\beta\beta}(t_{2h}^\beta - t_{1h}^\alpha) + h_{\alpha\beta}h_{2h}^\beta = 0, \\
(m_\beta^h \delta \mu_\beta - m_\beta^h \delta \mu_\beta) + h_{\beta\beta}(t_{2h}^\beta - t_{1h}^\beta) + h_{\beta\beta}h_{2h}^\beta = 0, \\
(m_\alpha^h \delta \mu_\alpha - m_\beta^h \delta \mu_\beta) + h_{\alpha\alpha}(2m_\alpha^h - t_{1h}^\alpha + t_{2h}^\alpha) + h_{\alpha\beta}h_{2h}^\beta = 0, \\
\alpha \beta 
\end{align*}
\]

(125)

Here we replace each difference $\delta \mu_{p\rho}$ by $\delta \mu_p$, as in Sec. \[ \text{[V]} \] omit the common index $n=m=1$ at $h_{n\rho}$ and $m_{p\rho}$: $h_{n\rho} = h_{1\rho}^n$, $m_{p\rho} = m_{1\rho}^p$; and use Eq. \[ \text{[3]} \] to express $\beta_{1p}$ via one-site and two-site averages, $t_{1p}^\lambda$ and $t_{2p}^\lambda$.

Writing Eqs. \[ \text{[3]} \] for fluxes $J_{0\rightarrow 1}^c$ in a ternary alloy, it is convenient to use the identity

\[
m_\rho^c + m_\rho^c + m_\rho^h = -\delta \rho
\]

(126)

which is the evident generalization of Eq. \[ \text{[27] \} for a binary alloy. Then Eqs. \[ \text{[3]} \] can be written as follows:

\[
\begin{align*}
-T_{J_{0\rightarrow 1}^c} = w_{0}^c \delta \mu_\alpha - 2m_\alpha^h h_{\alpha\alpha} + 2m_\beta^h (h_{\beta\beta} + h_{\alpha\beta} - h_{\alpha\alpha}), \\
-T_{J_{0\rightarrow 1}^c} = w_{0}^c \delta \mu_\beta = 2m_\beta^h (h_{\alpha\alpha} + h_{\alpha\beta} - h_{\beta\beta}), \\
-T_{J_{0\rightarrow 1}^c} = c_{m_\alpha} \delta \mu_\alpha + 2m_\alpha^h h_{\alpha\alpha} + 2m_\beta^h h_{\beta\beta} (127)
\end{align*}
\]

where we also take into account relations \[ \text{[23]} \] and \[ \text{[28]} \].

In Eqs. \[ \text{[125]-[127]} \], the tracer self-diffusion corresponds to $h = A$, $\beta = B$, $\alpha = A^*$, and the tracer solute diffusion, to $h = A$, $\beta = B$, $\alpha = B^*$. Each tracer diffusion coefficient $D_{p*}$, with $p*$ equal to $A^*$ or $B^*$ can be written in the general form \[ \text{[110]} \] with replacing $p$ by $p^*$ and the correlation factor $r_{p*}$ which corresponds to the terms with fields $h_{p*}$ in Eqs. \[ \text{[127]} \]. The enhancement factor $b_{p*}$ is defined by the usual relation:

\[
D_{p*}(c) = D_{p*}(1 + c b_{p*})
\]

(128)

and, as in Eq. \[ \text{[110]} \], it includes three different terms:

\[
b_{p*} = b_{p*}^\alpha + b_{p*}^\beta + b_{p*}^{\alpha\beta}.
\]

(129)

Here the frequency enhancement factor $b_{p*}^{\alpha\beta}$ was discussed in Sec. \[ \text{[V]} \] while the correlation enhancement factor $b_{p*}^\alpha$ and the activity enhancement factor $b_{p*}^{\alpha\beta}$ (related to the activity $A_{p*}^{\alpha\beta}$) are defined similarly to $b_{p*}$ in \[ \text{[128]} \]:

\[
b_{p*} = \frac{\partial}{\partial c} \ln b_{p*}(c), \quad b_{p*}^{\alpha\beta} = \frac{\partial}{\partial c} \ln A_{p*}^{\alpha\beta}(c)
\]

(130)

where the lower index “0” means the $c \rightarrow 0$ value of the derivative, and we take into account that $A_{p*}^{\alpha\beta}(0) = 1$.

### B. Calculation of enhancement factor for tracer self-diffusion in a dilute binary alloy

For the tracer self-diffusion, we should put in Eqs. \[ \text{[125]} \] $h = A$, $\beta = B$, $\delta \mu_p = 0$, and $\alpha = A^*$, but to make formulas compact, we will also employ symbol $\alpha$ instead of $A^*$. We consider the case of a low site fraction of solute: $c \ll 1$, and the tracer site fraction $c_\alpha$ in the real experiments is low, too. However, Eqs. \[ \text{[125]} \] can be easily solved for any $c_\alpha$ which enables us to discuss also some methodical problems. Thus at first we consider the case of the arbitrary $c_\alpha$.

Let us discuss different terms in \[ \text{[129]} \]. The frequency enhancement factor $b_{p*}^\alpha$, is defined by Eqs. \[ \text{[113]} \] and \[ \text{[70]} \] and, as atoms $A^*$ and $A$ are chemically identical, it coincides with that for chemical diffusion given by the first equation \[ \text{[110]} \]. The activity enhancement factor $b_{p*}^{\alpha\beta}$ can be found from Eqs. \[ \text{[109]} \] and \[ \text{[177]} \] with replacing $B$ by $A^*$, which implies: $A_{p*}^{\alpha\beta} = 1$, $b_{p*}^{\alpha\beta} = 0$ Thus only the correlation enhancement factor $b_{p*}^\alpha$, should be calculated.

Expressing averages $m_{1p}^\lambda$, $t_{1p}^\lambda$, and $t_{2p}^\lambda$ in \[ \text{[125]} \] via reduced quantities $\tilde{m}_{1p}^\lambda$, $\tilde{t}_{1p}^\lambda$, and $\tilde{t}_{2p}^\lambda$ defined in \[ \text{[78]-[81]} \] and replacing index $\alpha$ in these quantities by index $A$ due to the chemical identity of atoms $A^*$ and $A$, we can write Eqs. \[ \text{[125]} \] for the tracer self-diffusion at low $c$ as follows:

\[
\begin{align*}
\tilde{m}_{1p}^\alpha(\delta \mu_\alpha - \delta \mu_A) + h_{\alpha\alpha}(2m_{1p}^\alpha - t_{1A}^\alpha) + c_{\alpha h} B_{1p}^\alpha = 0, \\
-\tilde{m}_{1p}^\alpha \delta \mu_A + h_{\alpha\alpha} c_{\alpha A}(t_{2A}^\alpha - t_{1A}^\alpha) + h_{\alpha B} c_{\alpha x}(2m_{1p}^\alpha - t_{1A}^\alpha) = 0, \\
\tilde{m}_{1p}^\beta \delta \mu_A + h_{\beta\beta} c_{\beta A}(t_{2A}^\beta - t_{1A}^\beta) + c_{\alpha A}(t_{2A}^\alpha - t_{1A}^\alpha) + h_{\alpha B} c_{\beta x}(t_{2A}^\beta - t_{1A}^\beta) = 0
\end{align*}
\]

(131)
while Eqs. [127] for fluxes take the form:

\[-T J^0_{0+1} = \omega_A [\alpha_c \delta \mu_A - 2 \alpha_c c_A \tilde{m}^A_h \alpha_v] + 2 \alpha_c c_A \tilde{m}^A_h (h_{Bv} + h_{AB} - h_{\alpha_v}) , \]

\[-T J^A_{0+1} = \omega_A [\alpha_c \delta \mu_A + 2 \alpha_c c_A \tilde{m}^A_h \alpha_v] + 2 \alpha_c c_A \tilde{m}^A_h h_{Bv} , \]

\[-T J^B_{0+1} = 2 \alpha_c \omega_B \tilde{m}^B_h (c_A (h_{\alpha_v} - h_{AB} - h_{Bv}) - c_A h_{Bv}) . \]

(132)

Explicit expressions for coefficients \( \tilde{m}^p_1, \tilde{t}^p_1 \) and \( \tilde{t}^p_2 \) needed to solve Eqs. (131) and (132) at low \( c \) can be found using Eqs. (77), (96), (111) and (113):

\[ \tilde{m}^A = -1 + c(3 f_u - 2 f_{AB}) , \quad \tilde{t}^A_1 = 9 - c(7 f_u + 2 f_{AB}) , \]

\[ \tilde{t}^A_2 = (6 x_1 + x_4) , \quad \tilde{m}^B = (2 x_1 - 3 x_4) , \quad \tilde{t}^A_2 = -7 , \quad \tilde{m}^B = -1 , \quad \tilde{t}^B_1 = 9 , \quad \tilde{t}^B_2 = (2 x_1 + 7 x_4) . \]

(133)

Taking into account the Gibbs-Duhem relation [103] for \( A \) and \( A^* \) atoms:

\[ c_A \delta \mu_A + c_A \delta \mu_A = 0 \]

and the relation \( c_A + c_A = (1 - c) \geq 1 \), we can express \( \delta \mu_A \) and \( \delta \mu_A \) in (131) via the difference \( \delta \mu = \delta \mu_A - \delta \mu_A \):

\[ \delta \mu_A = c_A \delta \mu , \quad \delta \mu_A = -c_A \delta \mu . \]

(135)

Then sum of two last equations and the first equation in the system (131) yield two equations for \( h_{\alpha v} \) and \( h_{\alpha B}^r \):

\[ \tilde{m}^A_h \delta \mu + h_{\alpha v} (2 \tilde{m}^A - x_1^2) + h_{\alpha B} (\tilde{t}^A + x_1^2) = 0 , \]

\[ \tilde{m}^B_h \delta \mu + h_{\alpha v} (2 \tilde{m}^B - x_1^2) + c_A ch_{\alpha B} (\tilde{t}^A + x_1^2) = 0 . \]

(136)

Solving Eqs. (131) and (136) up to the first order in \( c \), we can write each field \( h_{\alpha v} \) as \( h_{\alpha v} = h_{\alpha v}^0 + c_A h_{\alpha v}^1 \). Contributions of these fields to fluxes \( J_{0+1} \) in (132) include terms \( h_{\alpha v}^0, h_{\alpha v}^1, h_{\alpha B}^0, h_{\alpha B}^1 \), and \( \alpha B \) given by such expressions:

\[ h_{\alpha v}^0 = -\delta \mu / 11 , \quad h_{\alpha v}^0 = c_A (h_{\alpha v}^0 - h_{\alpha B}^0) , \]

\[ h_{\alpha B}^0 = -\delta \mu / 9 (2 x_1 + x_2 - 3 x_4) / 11 (2 x_1 + 9 x_2 + 7 x_4) , \]

\[ h_{\alpha B}^1 = 20 (x_1 - x_4) h_{\alpha v}^0 - (6 x_1 + x_4) h_{\alpha B}^0 / 11 . \]

(137)

Now we note that for the tracer self-diffusion with any tracer site fraction \( c_A \), both the total flux of \( A \) and \( A^* \) atoms and the flux of \( B \) atoms should be absent [8]:

\[ J_{0+1}^A + J_{0+1}^B = 0 , \quad J_{0+1}^B = 0 . \]

(138)

Using Eqs. (132), we see that both relations (138) hold true for the solutions (137). It illustrates the theoretical consistency of these solutions.

Going to the physical results, we consider the realistically low tracer site fractions \( c_A \ll 1 \). Substituting solutions (137) into the first equation (132) using Eq. (89) to relate quantity \( J_{0+1}^B \) to the flux \( J^A \), and Eq. (102) (with replacing \( B \rightarrow A^* \)), to relate this flux to the tracer diffusion coefficient \( D_{A^*} \), we obtain:

\[ D_{A^*} = a_{\alpha}^2 \omega_A J^0_{A^*} (1 + c b_{A^*}) . \]

(139)

Here \( f_{A^*}^3 = 9/11 \) is the well-known value of the tracer self-diffusion correlation factor in the NNJA used [8], while the correlation enhancement factor \( b_{A^*}^c \) is:

\[ b_{A^*}^c = -2 \frac{2}{9} - \frac{4}{11} \left[ (2 x_1 - 3 x_4) + \frac{2 (8 x_1 - 17 x_4)^2}{9 (2 x_1 + 9 x_2 + 7 x_4)} \right] . \]

(140)

The frequency enhancement factor \( b_{A^*}^f \) was mentioned to coincide with \( b_{A^*}^c \) in (116):

\[ b_{A^*}^f = (4 x_1 + 14 x_4 - 18 + b_{vB}^f) \]

(141)

with \( b_{vB}^f \) given by Eq. (117), while the activity term \( b_{A^*}^a \) in (129) is zero. Therefore, the total self-diffusion enhancement factor \( b_{A^*} \) (128) has the form

\[ b_{A^*} = b_{A^*}^a + b_{A^*}^c \]

(142)

with \( b_{A^*}^a \) and \( b_{A^*}^c \) given by Eqs. (131) and (140).

Presence of vacancy-solute term \( b_{vB} \) in Eqs. (131) and (132) implies, in particular, that the vacancy-solute binding energies \( -v_{vB}^2 \) can hardly be as high as those found recently for some plausible models [14, 15]. For example, value \( -v_{vB}^2 \sim 0.26 \) eV suggested in [15] for alloys AgSb at \( T \) between 1048 and 890 K corresponds to \( b_{vB} \) between (200) and (350) which can hardly be compatible with the experimental \( b_{A^*} \) between about 30 and 50, even if the entropy terms discussed in [15] (and disregarded in the five-frequency model) are taken into account. Values \( -v_{vB}^2 \) in the interval 3-100 meV given in Table III below and typical for theoretical estimates [10] seem to be more realistic.

C. Discussion of previous calculations of \( b_{A^*} \)

Previous calculations of \( b_{A^*} \) using both the traditional methods [2, 4, 5, 8] and the Monte Carlo simulations [23, 24] were reviewed in detail by Nastar together with her original results [11]. Let us first compare our results with those of Nastar obtained using her version of the master equation approach. There are two differences between our results in Eqs. (140) and (142) and those of Nastar given by Eqs. (56) and (57) in [11].

(i) The frequency enhancement factor \( b_{A^*}^c \) in (131) includes the vacancy-solute interaction term \( b_{vB} \) which is absent in the analogous Eq. (56) in [11].

(ii) The constant term \( -2/9 \) in the expression (140) for \( b_{A^*}^c \) is absent in the analogous Eq. (57) in [11].

Disagreement (i) seems to be due to the general shortcoming of the approach used by Nastar [11] mentioned in Secs. II and V, which is related to the employing for finding of statistical averages of some indirect considerations rather than the direct calculations. Disagreement (ii) can be related just to a numerical error.

In Fig. 3 (where we use the data shown in Figs. 1-5 of Ref. [11]), the results of various calculations of \( b_{A^*} \) are compared with the available Monte Carlo simulations.
FIG. 3: (color online) Dependencies of the tracer self-diffusion enhancement factor $b_A$ on $x_2$ at various $x_1$ and $x_4$ in [11] in the absence of vacancy-solute term $b_{bB} = 0$ in [11]. Symbol MC correspond to Monte Carlo simulations, and symbols L, HM, IK, N and PW, to Refs. [2, 3, 5, 11], and the present work, respectively. Different frames correspond to the following values of $x_1$ and $x_4$ and the following MC simulations: (a) $x_1 = 2$, $x_4 = 1$, [2]; (b) $x_1 = x_4 = 0.1$, [3]; (c) $x_1 = 10x_2$, $x_4 = 0.1$, [11]; (d) $x_1 = x_4 = x_2$, [11]. In frames (c) and (d), curves N and PW merge within accuracy of drawing.

Note that the scale of parameters $x_n$ used in these simulations usually differs from that typical for the real alloys for which $x_n$ and $b_{A^*}$ usually obey the relations [5, 9]:

$$x_1, x_4 \geq 1, \quad x_2 \gg 1, \quad |b_{A^*}| \gg 1.$$  \hspace{1cm} (143)

The realistic relations (143) are approximately obeyed only for $x_n$ values used in frame [3], and for this frame, our calculations of $b_A^*$ agree with the Monte Carlo simulations better than other calculations. For the rest frames [3, 3d], our calculations also usually agree with the Monte Carlo simulations better than other calculations, but the relatively small scale of the correlation term: $b_A^* \ll b_{A^*}$, makes differences between different results to be less pronounced. Note also that calculations of $b_{A^*}$ by Howard and Manning [4] (used in the most of estimates of parameters of five-frequency model for real alloys [2, 9]) usually differ from Monte Carlo simulations stronger than those in [11] and in the present work.

The comparison of relations (143) with (142) seems to imply that the main contribution to $b_{A^*}$ is usually made by the frequency term $b_{A^*}^c$, while the correlation term $b_{A^*}^p$ is less important. It can be related to the presence in Eq. (141) of large numerical factors both in the first two terms, $(4f_{AA} + 14f_n)$, and in the third term, $b_{bB}(\pm 12 f_{EB})$. Thus taking into account the vacancy-solute term $b_{bB}$ missed in the previous calculations seems to be necessary for realistic calculations of $b_{A^*}$.

VII. ENHANCEMENT OF TRACER SOLUTE DIFFUSION IN A DILUTE BINARY ALLOY

A. General equations for tracer solute diffusion in a binary alloy

Considering tracer solute diffusion, we put in Eqs. (125) $h = A$, $\alpha = B$, $\delta_A = 0$, and $b = B^*$, but again we will also employ a compact symbol $b$ instead of $B^*$.

Expressing averages $m_{\gamma}^B$, $t_{\gamma A}^B$, and $t_{\gamma p}^B$ in (125) via reduced quantities $\tilde{m}_{\gamma}^B$, $\tilde{t}_{\gamma A}^B$, and $\tilde{t}_{\gamma p}^B$, defined in (73-76), and replacing index $b$ with the chemical identity of atoms $B^*$ and $B$, we can write Eqs. (125) for tracer solute diffusion at any site fractions $c_B$ and $c_{B^*}$ as follows:

$$z\tilde{m}_{A^*}^{B} c_B \delta_{\mu_B} + c_B h_{\beta_B} \tilde{z}_{1A}^B + c_B (\tilde{z}_{2A}^B - \tilde{z}_{2B}^B) \] + c_B h_{B^*} (\tilde{z}_{1B}^A - \tilde{z}_{1A}^B) + c_B h_{B^*} \tilde{z}_{2B}^B = 0,$$

$$z\tilde{m}_{A^*}^{B} c_B \delta_{\mu_B} = 0,$$

$$c_B \delta_{\mu_B} \tilde{z}_{2B}^B = 0,$$

where $z = \omega_B/\omega_A$ is the same as in (124).

Atomic fluxes [12] for tracer solute diffusion have the following form:

$$\frac{-T \tilde{J}_{01}^B}{\omega_B} = \omega_B \{ c_B \delta_{\mu_B} - 2 c_B \tilde{t}_{1A}^B \} + c_B \delta_{\mu_B} \tilde{z}_{2B}^B,$$

$$\frac{-T \tilde{J}_{01}^B}{\omega_B} = \omega_B \{ 2 c_B \tilde{t}_{1B}^A (h_{B^*} - h_{B^*} + h_{B_B}) \},$$

$$\frac{-T \tilde{J}_{01}^B}{\omega_B} = \omega_B \{ c_B h_{B^*} \tilde{t}_{2B}^B \},$$

while coefficients $\tilde{m}_{\gamma}^B$, $\tilde{t}_{\gamma A}^B$, and $\tilde{t}_{\gamma p}^B$ in Eqs. (144) and (145) are defined by Eqs. (77), (78) and (80).

Summing two first equations (144) and taking into account the Gibbs-Duhem relation (11) for $B$ and $B^*$ atoms: $c_B \delta_{\mu_B} + c_B h_{B^*} = 0$, we find that fields $h_{B^*}$ in Eqs. (144) and (145) are related as follows:

$$c_B h_{B^*} \delta_{\mu_B} \frac{x_B}{x_A} + c_B h_{B^*} \frac{x_B}{x_A} = 0.$$  \hspace{1cm} (146)

Substituting this relation into Eqs. (145) we see that both the total flux of atoms $B$ and $B^*$ and the flux of atoms $A$ are absent at any site fractions $c_B$ and $c_{B^*}$:

$$\tilde{J}_{01}^B \delta_{\mu_B} + \tilde{J}_{01}^B = 0, \quad \tilde{J}_{01}^B = 0.$$  \hspace{1cm} (147)

Presence of these physically evident relations [analogous to (138)] for tracer self-diffusion [138] illustrates consistency of the theoretical approach used.

B. Calculation of enhancement factor for tracer solute diffusion in a dilute binary alloy

Below we calculate the tracer solute enhancement factor $b_{B^*}$ in a dilute binary alloy $AB$ for the realistically low values of tracer site fraction $c_B$: $c_B \ll c, c_B \ll 1$. Using Eq. (140) to express field $h_{B^*}$ via $h_{B^*}$, we can write Eqs. (141) for $h_{B^*}$ and $h_{B^*}$ as follows:

$$h_{B^*} \tilde{t}_{1B}^A (h_{B^*}^{} - h_{B^*}^{} + h_{B^*}) = z\tilde{m}_{B}^A \delta_{\mu_B},$$

$$h_{B^*} \tilde{t}_{2B}^A (h_{B^*}^{} - h_{B^*}^{} + h_{B^*}) = z\tilde{m}_{B}^A \delta_{\mu_B}.$$  \hspace{1cm} (148)

while Eq. (145) for the tracer flux $\tilde{x}_{B^*}$ takes the form

$$-T \tilde{J}_{01}^B = \omega_B c_B \delta_{\mu_B} - 2 c_B \tilde{t}_{1A}^B (h_{B^*} - h_{B^*}) + 2 c_B \tilde{t}_{1B}^A (h_{B^*} - h_{B^*}).$$  \hspace{1cm} (149)
To explicitly write flux $J^\beta$ in Eq. (149), we define the “reduced” fields $h^0_{\beta\nu}$, $h^1_{\beta\nu}$, and $h_1^0$ which correspond to solutions of Eqs. (118) in the zero-order and the first-order in $c$, respectively, and express $h_{\beta\nu}$ via $h^0_{\beta\nu}$:

$$h_{\beta\nu} = \delta_{\mu\nu}(2zB\mu A/D + ch^1_{\beta\nu}), \quad h^0_{\beta\nu} = z_0\tilde{m}_{B,0}A_D/D_0,$$

$$h^1_{\beta\nu} = [h^0_{\beta\nu}(\tilde{t}_1^{B,0} - 2\tilde{m}_{B,0} - \tilde{m}_{B,0}Aix)], \quad h^0_{\beta\nu} = h^0_{\beta\nu} \cdot 2\tilde{m}_{B,0}A_D/D_0. \quad (150)$$

where index \(0\) at each quantity indicates its value at $c = 0$, as in Eqs. (111) and (119), and $D$ [equal to $d_{11}^1$ in (93)] is the coefficient at $h_{\beta\nu}$ in the first equation (148):

$$D = (i_1^{B,0} - 2zB\mu A_D). \quad (151)$$

Using this notation and also Eqs. (39) and (102), we can write Eq. (149) in the form of relation for the tracer solute diffusivity $D_{\beta\nu}$ analogous to Eq. (110):

$$D_{\beta\nu} = a_0^2\omega_{B\nu} \cdot f_{B\nu} \cdot A_{B\nu}. \quad (152)$$

Due to the chemical identity of atoms $B^*$ and $B$, frequency $\omega_{B^*} = \omega_B$ in Eq. (152) is given by Eq. (106) for $\alpha = B$, the activity factor $A_{B^*}^{ac}$ coincides with that in Eqs. (106) and (107), and $f_{B^*}$ is the correlation factor:

$$f_{B^*} = \left[1 - zc_A(\tilde{m}_B)^2/D \right] + 2c(\tilde{m}_{B,0}\tilde{m}_{B,0} - \tilde{m}_{B,0}\tilde{m}_{B,0} - \tilde{m}_{B,0}\tilde{m}_{B,0}A_D). \quad (153)$$

Explicit expressions for the low-$c$ values of functions $z$, $\tilde{m}_B$, $\tilde{t}_1$, and $\tilde{t}_2^n$ in Eqs. (150) - (153) can be found using Eqs. (77), (90), (96), (104), and (111), and $f_{B^*}$ is the correlation factor:

$$f_{B^*} = \left[1 - zc_A(\tilde{m}_B)^2/D \right] + 2c(\tilde{m}_{B,0}\tilde{m}_{B,0} - \tilde{m}_{B,0}\tilde{m}_{B,0} - \tilde{m}_{B,0}\tilde{m}_{B,0}A_D). \quad (153)$$

$$f_{B^*} = \left[1 - zc_A(\tilde{m}_B)^2/D \right] + 2c(\tilde{m}_{B,0}\tilde{m}_{B,0} - \tilde{m}_{B,0}\tilde{m}_{B,0} - \tilde{m}_{B,0}\tilde{m}_{B,0}A_D). \quad (153)$$

$$f_{B^*} = \left[1 - zc_A(\tilde{m}_B)^2/D \right] + 2c(\tilde{m}_{B,0}\tilde{m}_{B,0} - \tilde{m}_{B,0}\tilde{m}_{B,0} - \tilde{m}_{B,0}\tilde{m}_{B,0}A_D). \quad (153)$$

where Mayer functions $f_{A\Delta}$, $f_{B^*}$, and $f_{A\nu}$ are the same as in (96), and $b_{BB}$ is the same as in (113). Eqs. (153), (154), and (119) show, in particular, that at $c \rightarrow 0$, the correlation factor for tracer solute diffusion is equal to that for chemical diffusion (3):

$$f_{B^*} = f_{B^*} = \left[1 - zc_A(\tilde{m}_B)^2/D \right] + 2c(\tilde{m}_{B,0}\tilde{m}_{B,0} - \tilde{m}_{B,0}\tilde{m}_{B,0} - \tilde{m}_{B,0}\tilde{m}_{B,0}A_D). \quad (153)$$

where $D_0 = (2x_1 + 2x_2 + 7x_4)$ is the same as in (113).

According to Eqs. (130) and (153), the correlation term $b_{B^*}$ in Eq. (129) can be written as the sum of two contributions, $b_{1B^*}$ and $b_{2B^*}$, which correspond to the second and the third term in Eq. (153):

$$b_{B^*} = b_{1B^*} + b_{2B^*},$$

$$b_{1B^*} = \frac{\partial}{\partial \tilde{c}_A} \left[zc_A(\tilde{m}_B)^2/D \right]_0,$$

$$b_{2B^*} = \frac{\partial}{\partial \tilde{c}_A} \left[zc_A(\tilde{m}_B)^2/D \right]_0 - \tilde{m}_{B,0}\tilde{m}_{B,0}A_D. \quad (156)$$

where $f_{BB}$ is given by Eq. (155).

Term $b_{1B^*}$ is the sum of three terms which correspond to three factors in square brackets in (150):

$$b_{1B^*} = -(2x_2/f_{BB}D_0)(l_1 + 2l_2 - l_3) \quad (157)$$

where $l_1$ is the appropriate logarithmic derivative:

$$l_1 = \frac{\partial}{\partial \tilde{c}_A} \ln(zc_A) \left|_{D_0} = (4y_1 - 4x_1 - 1 + b_{BB}) \right.,$$

$$l_2 = \frac{\partial}{\partial \tilde{c}_A} \ln(zc_A) \left|_{D_0} = 2y_1 - 3x_4 + 1 \right.,$$

$$l_3 = \frac{\partial}{\partial \tilde{c}_A} \ln(D_0) \left| = 2x_2(6y_1 - 4x_1 - 3x_4 + b_{BB}) \right. - 2x_1^2 - 7x_4^2 + D_0/D_0. \quad (158)$$

To find $b_{2B^*}$, we substitute expressions (150) for $h^0_{\beta\nu}$, $h^0_{\beta\nu}$, and (154) for $\tilde{m}_{B,0}$, into Eq. (150). It yields:

$$b_{2B^*} = \left\{ \frac{1}{f_{BB}} \left[ (6y_1 + x_4)x_2^2/D_0^2 \right. \right.$$

$$- \left( (3x_4 - 2y_1) + (6y_1 + x_4)x_2/D_0 \right)^2/(2y_1 + 7x_1) \right\}. \quad (159)$$

The total tracer solute enhancement factor is given by Eq. (129) with $p^* = B^*$. As the mean frequency $\omega_{B^*}$ and the activity factor $A_{B^*}^{ac}$ in (152) coincide with those for chemical diffusion, terms $b_{1B^*}$ and $b_{2B^*}$ in (129) can be found using Eqs. (110) and (107) for a binary alloy. Therefore, $b_{1B^*}$ is equal to $b_{1B^*}$ in (160):

$$b_{1B^*} = (4y_1 + 14x_4 - 18 + b_{BB}) \quad (160)$$

while expansion of Eq. (107) at low $c$ shows that $b_{1B^*}$ is equal to the quantity $b_{BB}$ in (118):

$$b_{1B^*} = -12f_{BB} - 6f_{BB} - \ldots \quad (161)$$

Thus the tracer solute enhancement factor $b_{B^*}$ can be written as

$$b_{B^*} = b_{1B^*} + b_{2B^*} + b_{2B^*} \quad (162)$$

where various terms are given by Eqs. (157) - (161).

Experimental values of $b_{1B^*}$ usually notable exceed unity: $|b_{1B^*}| > 1$, similarly, $b_{BB}$ values (6). As in the case of $b_{BB}$ discussed above, these large values can imply that the main contribution to $b_{BB}$ is made by the frequency and activity terms in (102), $b_{BB}$, and $b_{BB}^{ac}$, as expressions (160) and (107) include large numerical factors, while contributions of correlation terms $b_{1B^*}$ and $b_{2B^*}$ in the total $b_{BB}$ are usually less significant.

### VIII. ESTIMATES OF PARAMETERS OF FIVE-FREQUENCY MODEL FOR REAL ALLOYS

Basic parameters of five-frequency model, $x_1$, $x_2$, and $x_4$ or frequency ratios $w_2/w_1$, $w_3/w_1$ and $w_4/w_0$ in...
can be estimated from experimental data about the ratio of tracer diffusion coefficients, \( R^*_D = D^*_B / D^*_A \), the solute correlation factor \( f_{BB} \), and the vacancy flow factor \( G = L^{0}_{AB} / L^{0}_{BB} \) [3, 9]. Then data about the tracer solvent enhancement factor \( b_A \) described by Eqs. [140]-[142] enable us to estimate the vacancy-solute interaction if we suppose it to be short-ranged: \( b_{BB} = -12f_{1}^{B} \).

In Table III we present estimates of \( x_n \) and \( v^{B}_0 \) for several alloys for which data about \( R^*_D, f_{BB}, G \) and \( b_A \) are available. For alloys AgZn, we present \( G \) estimated from electromigration data in Ref. [23]. For alloys AlZn, we are not aware of data about \( b_A \), thus for \( f_{1}^{B} \) we give its expression via this unknown \( b_A \). To calculate \( R^*_D \) and \( f_{BB} \), we use the following relations:

\[
R^*_D = x_2 f_{BB} / f_0, \quad G = L^{0}_{AB} / (1 - L^{0}_{BB})
\]

where \( f_0 = 0.7815 \) is the exact correlation factor for tracer self-diffusion [3], while \( f_{BB} \) and \( L^{0}_{BB} \) are given by Eqs. [119]-[122] with \( P_N \) and \( P_B \) taken from [8]. For the tracer enhancement factor \( b_A \) we used Eqs. [140]-[142]. Errors in estimates of interactions \( v^{B}_0, u^{B}_1 \) and \( \Delta^B \) in Table III for Cu-based and Ag-based alloys correspond to the variations of \( |G| \) by \( \pm 10\% \), while for AlZn alloys these errors correspond to \( \delta G = \pm 0.13 \) in [16].

| Alloy   | \( T, \) K | \( R^*_D \) | \( f_{BB} \) | \( G \) | \( b_A \) | Source of data | Parameters | Interactions, meV |
|---------|-------------|-------------|-------------|-------|---------|----------------|------------|------------------|
| CuZn   | 1168        | 3.56        | 0.47        | -0.22 | 7.3     | [8, 9]        | \( x_1 \)   | \( x_2 \)  | \( x_4 \)  | \( v^{B}_1 \) | \( u^{B}_1 \) | \( \Delta^B \) |
| CuCd   | 1076        | 10.2        | 0.22        | -0.7  | 35      | [8, 9]        | 5.1        | 36    | 2.5    | 0.1     | -9\( \pm \)23 | 85\( \pm \)12 | 18\( \pm \)31 |
| CuIn   | 1089        | 12          | 0.07        | -0.57 | 43      | [8, 9]        | 4.2        | 134   | 3.0    | -0.12   | 12\( \pm \)31 | 105\( \pm \)10 | 74\( \pm \)30 |
| CuSn   | 1089        | 14.1        | 0.15        | -0.84 | 48      | [8, 9]        | 6.6        | 73    | 3.4    | 0.57    | -42\( \pm \)27 | 115\( \pm \)18 | 52\( \pm \)48 |
| CuSn   | 1014        | 17          | 0.15        | -1.06 | 40      | [8, 9]        | 9.6        | 89    | 3.2    | 1.8     | -88\( \pm \)28 | 102\( \pm \)27 | 6\( \pm \)67  |
| AgZn   | 1153        | 3.9         | 0.57        | -0.39 | 12.7    | [9, 25]       | 3.1        | 5.3   | 1.8    | 0.52    | -42\( \pm \)5   | 59\( \pm \)5   | 6\( \pm \)14  |
| AlZn   | 829         | 3.5         | 0.5         | -0.19 |         | [16]          | 2.2        | 5.5   | 1.4    | (9.8 \( - b_A \))/12 | 23\( \pm \)9  | -9\( \pm \)29  |

Before to discuss physical implications of results presented in Table IV we note that, according to usual ideas [3], an increase in the excess of the valency and atomic volume of impurity, \( Z_B \) and \( \bar{v}_B \), with respect to those of host atoms, \( Z_A \) and \( \bar{v}_A \), should lead, first, to the increase of the vacancy-solute attraction as both the Coulomb and elastic interactions become stronger and, second, to the increase of the ratio \( x_2 = \omega^0_B / \omega^0_A \) as the activation energy \( E^{BC}_B \) in [10] should decrease as potential minima for a \( B \) atom in the host lattice at high \( \bar{v}_B / \bar{v}_A \) should become more shallow. Hence in the sequence of alloys CuZn-CuCd-CuIn-CuSn we can expect, generally, an increase of both the vacancy-solute attraction \( -v^{B}_1 \) and the activation frequency ratio \( x_2 \), as well as the increase of this ratio with lowering temperature \( T \).

The results for Cu-based alloys in Table III, generally, agree with these considerations (except CuIn alloys for which the experimental value \( f_{BB} \) seems to be anomalously low while errors in \( v^{B}_1 \) are rather large). It can confirm that the five-frequency model describes these alloys reasonably (even though it neglects many physical effects, in particular, the long-ranged stress-induced interactions which should be particularly important at high \( \bar{v}_B / \bar{v}_A \) [18]). The kinetic interaction \( u^{B}_1 \) defined by Eq. [15] also increases in this sequence of alloys which again seems to be natural. The saddle-point interactions \( \Delta^B \) in Table III are usually weaker than kinetic ones, and their changes with \( Z_B / Z_A \) and \( \bar{v}_B / \bar{v}_A \) seem to be less pronounced.

Expressions [101] - [102] for the tracer solute enhancement factor \( b_{BB} \) include also term \( b_{BB} \) which can be estimated from thermodynamic data, see, e. g. [26], and term \( y_1 \) in [113]. Hence data about \( b_{BB} \) enable one to estimate the solute-solute saddle-point interaction \( \Delta^B \). It will be shown elsewhere that the same six parameters: \( x_1, x_2, x_4, b_{BB}, b_{BB} \) and \( y_1 \), fully describe also the chemical (intrinsic) diffusion enhancement factors, \( b_A \) and \( b_B \), for the five-frequency model.

Unfortunately, we are not aware of reliable data about \( b_{BB} \) in the “fully-described” alloys (such as those in Table III) for which data about \( R^*_D, f_{BB}, G \) and \( b_A \) are available. For example, Ref. [26] includes data about...
both tracer and intrinsic diffusion coefficients, \(D_p^* (c)\) and \(D_p (c)\), for CuZn at \(T = 1053\) K and AgCd at \(T = 873\) K. However, values of \(b_A^*\) in these data strongly differ from those obtained by other authors at similar temperatures \(8, 3\), and the necessary relation \(D_p^0 = D_B^0\) is notably violated. The reliable data about \(D_B^0, D_A^0\) and \(D_B^0\) in the “fully-described” FCC alloys will allow to estimate all six microscopic parameters of the theory.

IX. CONCLUSIONS

Let us summarize the main results of this work. We present the new formulation of the master equation approach to the theory of diffusion in substitution alloys using the five-frequency model of FCC alloys as an example. Unlike the earlier version of this approach suggested by Nastar et al. \[10-12\], our formulation gives the explicit form for all equations of the theory and uses the well-elaborated methods of statistical physics to approximately solve these equations. The approach developed is used to calculate the enhancement factors for tracer solvent and tracer solute diffusion in dilute FCC alloys. We show that some significant contribution to the tracer solvent enhancement factor related to the vacancy-solute interaction was missed in the previous treatments of this problem. It implies that existing estimates of parameters of five-frequency model for the most of real alloys should be revised. For several FCC alloys for which necessary experimental data are available, we estimate these parameters, including the vacancy-solute interaction. The results obtained seem to show that the five-frequency model for these alloys is adequate. We also discuss the experiments needed to fully describe both tracer and chemical diffusion in FCC alloys in the framework of the five-frequency model.

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[1] A. B. Lidiard, Phil. Mag. 46, 1218 (1955).
[2] A. B. Lidiard, Phil. Mag. 5, 1171 (1960).
[3] J. R. Manning, Phys. Rev. 136, A1758 (1964).
[4] R. E. Howard and J. R. Manning, Phys. Rev. 154, 561 (1967).
[5] J.-L. Bocquet, Acta Metall. 20, 1347 (1974).
[6] A. D. Le Claire, J. Nucl. Mat. 69-70, 70 (1978).
[7] S. Ishioka and V. Koiva, Phil. Mag. A 50, 505 (1984).
[8] A.R. Alnatt and A. B. Lidiard, Atomic Transport in Solids (Camb. Univ. Press, 1993).
[9] J.-L. Bocquet, G. Brebec, Y. Limoge, in: Physical Metallurgy; fourth edition, eds. R. W. Cahn and P. Haasen (Elsevier Science BV, 1996), p. 535.
[10] M. Nastar, V. Yu. Dobretsov and G. Martin, Phil. Mag. A 80, 155 (2000).
[11] M. Nastar, Phil. Mag. 85, 3767 (2005).
[12] V. Barbe and M. Nastar, Phil. Mag. 86, 1513 (2006).
[13] F. Soisson and C.-C. Fu, Phys. Rev. B 76, 214102 (2007).
[14] F. Faupel, C. Kostler, K. Bierbaum and Th. Hehenkamp, J. Phys.: Met. Phys. 18, 205 (1988).
[15] H. Hagenschulte and Th. Heumann, J. Phys.: Condens. Matter, 1985 (1989).
[16] H. Hagenschulte and Th. Heumann, J. Phys.: Condens. Matter, 3601 (1994).
[17] K. D. Belashchenko and V. G. Vaks, J. Phys.: Condensed Matter 10, 1965 (1998).
[18] V.G. Vaks, I.A. Zhuravlev, JETP 115, 634 (2012).
[19] K. Yu. Khromov, F. Soisson, A.Yu. Stroev, V.G. Vaks, JETP 139, 479 (2011).
[20] V.G. Vaks, G. D. Samolyuk, JETP 88, 89 (1999).
[21] V.G. Vaks, K. Yu. Khromov, JETP 106, 94 (2008).
[22] V.G. Vaks, I.A. Zhuravlev and K.Yu. Khromov, JETP 111, 796 (2010).
[23] I. V. Belova and G. E. Murch, Phil. Mag. 83, 377 (2003).
[24] I. V. Belova and G. E. Murch, Phil. Mag. 83, 393 (2003).
[25] N. V. Doan and J.-L. Bocquet, Thin Solid Films 25, 15 (1975).
[26] N. S. Kulkarni, Ph.D. Dissertation, Univ. of Florida, Gainesville, 2004.
