ЖЭТФ, 2012, том 142, вып. 4 (10), стр. 719–737

STATISTICAL DERIVATION OF BASIC EQUATIONS OF DIFFUSIONAL KINETICS IN ALLOYS WITH APPLICATION TO THE DESCRIPTION OF DIFFUSION OF CARBON IN AUSTENITE

V. G. Vaks**, *I. A. Zhuravlev

National Research Center "Kurchatov Institute"
123182, Moscow, Russia

Moscow Institute of Physics and Technology (State University)
117303, Moscow, Russia

Received January 26, 2012

Basic equations of diffusional kinetics in alloys are statistically derived using the master equation approach. To describe diffusional transformations in substitution alloys, we derive the "quasi-equilibrium" kinetic equation that generalizes its earlier versions by taking possible "interaction renormalization" effects into account. For the interstitial alloys Me–X, we derive an explicit expression for the diffusivity D of an interstitial atom X. This expression notably differs from those used in previous phenomenological treatments. This microscopic expression for D is applied to describe the diffusion of carbon in austenite based on some simple models of carbon–carbon interaction. The results obtained enable us to make certain conclusions about the real form of these interactions and about the scale of the "transition state entropy" for diffusion of carbon in austenite.

1. INTRODUCTION

The problem of development of a adequate theoretical description of diffusion in alloys attracts interest from both fundamental and applied standpoints, see, e. g., [1–15]. Presently, this description is usually based on the phenomenological theory of diffusion in multicomponent systems developed by Onsager many years ago [6]. Phenomenological kinetic coefficients are calculated in this theory using various simplified models with parameters estimated empirically [1–4]. However, these empirical models have usually no consistent theoretical justification, and their relation to interatomic interactions, as well as the possibilities of their application to other alloy systems, are typically not clear.

An important problem in this field is the strong concentration dependence of the diffusivity D of carbon in austenite [1–5]. This dependence causes complications in the kinetic analysis of various diffusion-controlled reactions in steels [4], and several empirical models have been suggested to describe this dependence [1–4]. However, it is generally unclear whether these models can be used for predictions of D at temperatures $T \lesssim 1000$ K (where many important phase transformations occur but D cannot be directly measured because austenite is unstable here) or under partial substitution of iron by other metals [5].

A consistent statistical description of the diffusional kinetics in alloys can be based on the master equation approach [7–15]. This approach allows expressing the phenomenological kinetic coefficients, such as the mobility M_α of an α-species atom, in terms of interatomic interactions in an alloy. These interactions can be estimated using either some microscopic models [16–18] or *ab initio* methods [14, 19, 20]. As the level of accuracy and reliability of *ab initio* calculations is steadily increasing, this microscopic approach seems to be prospective for nonempirical calculations of diffusivitiy.

At the same time, previous considerations of diffusional kinetics in alloys based on the master equation approach were usually restricted by discussions of only simplest models and approximations or some particular problems [7–9, 11, 13]. On the other hand, several more general discussions [10, 15] included many unnecessary complications and restrictions that can hinder the understanding of the results. Therefore, the first aim of this paper is to present a clear and general derivation

*E-mail: vaks@mbslab.kiae.ru

of basic equations of diffusion in alloys based on the master equation approach, for both substitution and interstitial alloys.

For this, in Sec. 2, we first discuss the vacancy-mediated kinetics under diffusional transformations in substitution alloys. This problem has been considered in Ref. [15], and some equations derived in Sec. 2 have been already presented there. But the full derivation of these equations has not been given in [15], while the similar derivation in [10] includes a number of complications and inaccuracies. In Sec. 2, we also discuss the methods of computer simulations based on the microscopic equations proposed, including some generalizations of the previously discussed "equivalence theorem" [10, 15], which greatly simplifies such simulations. In Sec. 3, we consider interstitial Me–X alloys and derive the general statstical expression for the diffusivity D of an interstitial atom X in a simple and physically transparent form. This expression involves only microscopic parameters that can be estimated using either theoretical models or *ab initio* calculations. We also generalize this microscopic expression for D to the case of multicomponent alloys ($Me_1Me_2\ldots$)-X with several species atoms in the metal sublattice.

The second aim of this work is to apply the results in Sec. 3 to treat the above-mentioned problem of diffusion of carbon in austenite microscopically. This treatment described in Sec. 4 is based on the microscopic model of carbon–carbon (C–C) interactions in austenite suggested by Blanter [16], which supposes a strong "chemical" repulsion at short C–C distances R_{CC} and a purely deformational (or "strain-induced") interaction at longer R_{CC} distances. We show that some natural generalizations of this model allow describing both thermodynamic and diffusional characteristics of carbon in austenite at the same level of accuracy as that achieved in phenomenological models [1–4, 36]. The microscopic approach simultaneously allows making a number of conclusions about the type of C–C interactions and about some physical features of diffusion of carbon in austenite. The main results of this work are summarized in Sec. 5.

2. EQUATIONS OF VACANCY-MEDIATED KINETICS FOR DIFFUSIONAL TRANSFORMATIONS IN SUBSTITUTION ALLOYS

2.1. General equations for mean occupations of lattice sites

We first present the necessary relations from Ref. [15] with some extensions and comments. We consider a substitutional alloy with $m+1$ components p', including atoms of m different species $p = p_1$, $p_2, \ldots, p_m$ and vacancies v: $p' = \{p, v\}$. The distributions of atoms over the lattice sites i are described by occupation number sets $\{n_i^{p'}\}$, where the operator $n_i^{p'}$ is 1 when the site i is occupied by a p'-species component and 0 otherwise. For each i, these operators obey the identity $\sum_{p'} n_i^{p'} = 1$, and hence only m of them are independent. It is convenient to let the independent operators be denoted by Greek letters ρ or σ: $(n_i^{p'})_{indep} = n_i^\rho$, with the rest operator, denoted as n_i^h, expressed via the n_i^ρ:

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

We note that both n_i^h and n_i^ρ are projection operators:

$$(n_i^h)^2 = n_i^h, \quad n_i^h n_i^\rho = 0, \quad n_i^\rho n_i^\sigma = \delta_{\rho\sigma} n_i^\rho. \tag{2}$$

For dilute alloys, it is convenient to set "h" in (1) to be the host component, e.g., h = Fe for the dilute BCC Fe–Cu–v alloys discussed in [14, 15] and used below for illustrations.

In terms of all operators $n_i^{p'}$, the total configurational Hamiltonian H^t (for simplicity supposed to describe pairwise interactions) can be written as

$$H^t = \frac{1}{2} \sum_{p'q',ij} V_{ij}^{p'q'} n_i^{p'} n_j^{q'}. \tag{3}$$

After elimination of the operators n_i^h in accordance with (1), this Hamiltonian becomes

$$\begin{aligned} H^t &= E_0 + \sum_{\rho i} \varphi_\rho n_i^\rho + H_{int}, \\ H_{int} &= \sum_{\rho\sigma, i>j} v_{ij}^{\rho\sigma} n_i^\rho n_j^\sigma \end{aligned} \tag{4}$$

which includes only independent n_i^ρ, while the constants E_0 and φ_ρ and the "configurational interactions" $v_{ij}^{\rho\sigma}$ are linearly expressed in terms of the couplings $V_{ij}^{p'q'}$ in (3), in particular,

$$v_{il}^{\rho\sigma} = (V^{\rho\sigma} - V^{\rho h} - V^{h\sigma} + V^{hh})_{ij}. \tag{5}$$

The fundamental master equation for the probability P of finding an occupation number set $\{n_i^\rho\} = \xi$ is [12]

$$\frac{dP(\xi)}{dt} = \sum_\eta [W(\xi,\eta)P(\eta) - W(\eta,\xi)P(\xi)] \equiv \hat{S}P \tag{6}$$

where $W(\xi,\eta)$ is the $\eta \to \xi$ transition probability per unit time. If we adopt the conventional "transition

state" model [14] for the probabilities W, we can express the transfer matrix $\hat{S}$ in (6) in terms of the probability of an elementary intersite exchange ("jump") $pi \rightleftharpoons vj$ between neighboring sites i and j:

$$W_{ij}^{pv} = n_i^p n_j^v \omega_{pv}^{eff} \exp\left[-\beta(\hat{E}_{pi,vj}^{SP} - \hat{E}_{pi,vj}^{in})\right], \qquad (7)$$

where $\beta = 1/T$ is the inverse temperature, $\hat{E}_{pi,vj}^{SP}$ is the saddle-point energy, $\hat{E}_{pi,vj}^{in}$ is the initial (before the jump) configurational energy of a jumping atom p and a vacancy, and the pre-exponential factor ω_{pv}^{eff} can be written as

$$\omega_{pv}^{eff} = \omega_{pv} \exp\left(\Delta S_{pi,vj}^{SP}\right). \qquad (8)$$

Here, ω_{pv} is the attempt frequency, which is generally expected to have the order of magnitude of the mean frequency of vibrations of a jumping atom in an alloy, and $\Delta S_{pi,vj}^{SP}$ is the entropy difference between the saddle-point and the initial alloy states. This difference is mainly due to the difference of atomic vibrations in the saddle-point state (supposed to be locally equilibrium, which allows thermodynamic notion such as the entropy to be applied to it) and the initial state. At high temperatures T under considerations (actually, already at $T \gtrsim \theta_D/2$, where θ_D is the Debye temperature [22]), this entropy difference can be described by the classical expression

$$\Delta S_{pv}^{SP} = 3 \ln \frac{\bar{\omega}_p^{in}}{\bar{\omega}_p^{sp}}, \qquad (9)$$

where $\bar{\omega}_p^{in}$ and $\bar{\omega}_p^{sp}$ are certain mean frequencies of vibrations of a jumping atom in the initial and saddle-point states (see, e. g., [29]). Because the frequencies ω_p^{sp} in the saddle-point configuration can notably soften with respect to ω_p^{in}, the entropy difference ΔS_{pv}^{SP} can be expected to take large positive values. For example, for the Fe–Cu–v alloys with the Debye frequency $\omega_D^{\mathrm{Fe}} \approx 6 \cdot 10^{13}\ \mathrm{sec}^{-1}$ [23], Soisson and Fu (SF) [14] found that $\omega_{\mathrm{Fe}\,v}^{eff} \sim 80\,\omega_D^{\mathrm{Fe}}$ and $\omega_{\mathrm{Cu}\,v}^{eff} \sim 30\,\omega_D^{\mathrm{Fe}}$. This implies that $\Delta S_{\mathrm{Fe}\,v}^{SP} \sim 4.5$, $\Delta S_{\mathrm{Cu}\,v}^{SP} \sim 3.5$, $\bar{\omega}_{\mathrm{Fe}}^{sp} \sim \omega_D^{\mathrm{Fe}}/4$, and $\bar{\omega}_{\mathrm{Cu}}^{sp} \sim \omega_D^{\mathrm{Fe}}/3$, although so high values of ΔS^{SP} and $\omega_D/\bar{\omega}^{sp}$ can be somewhat overestimated due to inaccuracies of the estimates [14].

The saddle-point energy $\hat{E}_{pi,vj}^{SP}$ depends in general on the atomic configuration near the ij bond. We describe this dependence by the SF model [14] assuming the saddle-point energy to depend only on occupations of lattice sites l nearest to the center of the ij bond (denoted by l_{nn}^{ij}):

$$\hat{E}_{pi,vj}^{SP} = \sum_{q,\, l=l_{nn}^{ij}} \varepsilon_q^p\, n_l^q = E_h^p + \hat{\Delta}_{ij}^p. \qquad (10)$$

Here, E_h^p is the saddle-point energy for the pure host metal and the operator $\hat{\Delta}_{ij}^p$ describes changes in this energy due to a possible presence of minority atoms near the bond:

$$E_h^p = z_{nn}^b \varepsilon_h^p, \quad \hat{\Delta}_{ij}^p = \sum_{\rho,\, l=l_{nn}^{ij}} \Delta_\rho^p n_l^\rho, \qquad (11)$$

where z_{nn}^b is the total number of nearest lattice sites l for each bond (which is $z_{nn}^b = 6$ for a BCC lattice), $\Delta_\rho^p = (\varepsilon_\rho^p - \varepsilon_h^p)$, and ε_ρ^p and ε_h^p are the microscopic parameters of pairwise interactions calculated by SF using *ab initio* methods [14]. We note that our definitions of $\hat{\Delta}_{ij}^p$ and Δ_ρ^p differ by sign from those used in [14] and [15].

The interaction parameters $V_{ij}^{p'q'}$, ε_h^p, and Δ_ρ^p in Eqs. (3) and (11) can be calculated by *ab initio* methods. For Fe–Cu–v alloys, this was shown in [14]. Theoretical calculations of the factors ω_{pv}^{eff} in Eq. (7) are more difficult due to the presence of the entropic factor $\exp(\Delta S^{SP})$ in Eq. (8). However, values of ω_{pv}^{eff} can be estimated from experimental data on self-diffusion and diffusion of isolated atoms in a host metal, as described in [14].

Because the n_i^ρ in Eqs. (1), (4), and (6) are projection operators obeying Eqs. (2), the most general expression for the probability $P = P\{n_i^\rho\}$ in (6) can be written in the form of the generalized Gibbs distribution [10–12]

$$P\{n_i^\rho\} = \exp\left[\beta\left(\Omega + \sum_{\rho i} \lambda_i^\rho n_i^\rho - H_{int} - \hat{h}_{int}\right)\right], \qquad (12)$$

$$\hat{h}_{int} = \frac{1}{2}\sum_{\rho\sigma,ij} h_{ij}^{\rho\sigma} n_i^\rho n_j^\sigma + \frac{1}{6}\sum_{\rho\sigma\tau,ijk} h_{ijk}^{\rho\sigma\tau} n_i^\rho n_j^\sigma n_k^\tau + \ldots \qquad (13)$$

Here, the parameters λ_i^ρ (which are both time and space-dependent in general) can be called "site chemical potentials" for ρ-species atoms; they are related to local chemical potentials μ_i^ρ and μ_i^h of ρ-species and host atoms as $\lambda_i^\rho = (\mu_i^\rho - \mu_i^h)$ [21]. In (12), H_{int} is the same as in (4); the parameters $h_{i\ldots j}^{\rho\ldots\sigma}$ in (13) (also depending on both time and space) describe possible renormalizations of interactions, and Ω is determined by normalization.

As discussed in detail in [12], under the usual conditions of phase transitions corresponding to the absence of external particle or energy fluxes (that is, when the alloy is a "closed" but not an "open" statistical system),

the effects of renormalizations of interactions can be expected to be insignificant, and we can therefore set

$$\hat{h}_{int} = 0 \tag{14}$$

in (12). There are at least two reasons to expect the validity of Eq. (14) for transformations in closed systems. First, this relation holds both before and after the transformation. For example, it is true before an initially equilibrated alloy is quenched from a higher temperature T_h to the lower temperature T_l corresponding to another equilibrium phase (or phases), and it is also true after the new equilibrium state at $T = T_l$ is reached. Therefore, there is no driving force drawing the correlation parameters $h^{\rho\ldots\sigma}_{i\ldots j}$ in distribution (12) away from their Gibbs values $h^{\rho\ldots\sigma}_{i\ldots j} = 0$. Second, the parameters $h^{\rho\ldots\sigma}_{i\ldots j}$ in distribution (12) mainly describe the short-range order. After a change of external conditions, such as temperature, this short-range order is established relatively fast, in a time of the order of one interatomic exchange time τ_a, while the time for completing microstructural evolution under phase transition is usually much longer, $t \gg \tau_a$ [8, 10, 15]. Therefore, possible fluctuative violations of relation (14) at small $t \lesssim \tau_a$ are not important for the whole evolution.

When relation (14) is satisfied, Eq. (12) takes the form

$$P\{n_i^\rho\} = \exp\left[\beta(\Omega + \sum_{\rho i} \lambda_i^\rho n_i^\rho - H_{int})\right], \tag{15}$$

which is called the "quasi-equilibrium Gibbs distribution" in what follows.

We note, however, that for the essentially "open" systems such as alloys under irradiation [24, 25] or an alloy with an external atomic flux imposed [11], quasi-equilibrium relation (14) can be strongly violated. Important cases of such violations can be the phase transitions accompanied by significant fluxes of vacancies into the transformation region, for example, the precipitation in Fe–Cu–v alloys, where these fluxes arise due to the strong trapping of vacancies by the copper-based precipitates [14]. In such cases, the effective vacancy–copper interactions can notably vary with the evolution time, and large renormalizations $h_{ij}^{v\mathrm{Cu}} \neq 0$ can be expected. Possible methods of calculations of such renormalizations have been discussed in [10, 11, 13].

Multiplying Eq. (6) by operators n_i^ρ and summing over all configurations $\{n_i^\sigma\}$, we obtain the set of equations for the mean occupations of sites ("local concentrations") $c_i^\rho = \langle n_i^\rho \rangle$:

$$\frac{dc_i^\rho}{dt} = \langle n_i^\rho \hat{S} \rangle, \tag{16}$$

where $\langle\langle(\ldots)\rangle\rangle = \sum_{\{n_j^\sigma\}}(\ldots)P\{n_j^\sigma\}$ means averaging over the distribution P, for example,

$$c_i^\rho = \langle n_i^\rho \rangle = \sum_{\{n_j^\sigma\}} n_i^\rho P\{n_j^\sigma\}. \tag{17}$$

In what follows, it is convenient to mark the minority atoms by Greek indices $\alpha, \beta, \ldots$ Then the index p in Eqs. (7)–(12) is α or h, corresponding to a minority or a host atom, and the index ρ in Eqs. (12)–(16) is α or v, corresponding to a minority atom or a vacancy. System of equations (16) can then be explicitly written as

$$\begin{gathered}
\frac{dc_i^\alpha}{dt} = \sum_{\{n_k^\rho\}} \sum_{j(i)} \omega_{\alpha v}^{eff} \times \\
\times \left[n_i^v n_j^\alpha \exp\left(\beta \hat{E}^{in}_{\alpha i, vj} - \beta \hat{E}^{SP}_{\alpha i, vj}\right) - \{i \to j\} \right] \times \\
\times \exp[\beta\,(\Omega - H_{eff})], \\
\frac{dc_i^v}{dt} = \sum_{\{n_k^\rho\}} \sum_{p} \sum_{j(i)} \omega_{pv}^{eff} \times \\
\times \left[n_i^p n_j^v \exp\left(\beta \hat{E}^{in}_{pi, vj} - \beta \hat{E}^{SP}_{pi, vj}\right) - \{i \to j\} \right] \times \\
\times \exp[\beta\,(\Omega - H_{eff})],
\end{gathered} \tag{18}$$

where the symbol $j(i)$ means summation over sites j that are nearest neighbors of the site i, and p is h or α, while $H_{eff} = H_{eff}\{n_k^\rho\}$ is the effective Hamiltonian for statistical averaging of expressions in square brackets:

$$\begin{gathered}
H_{eff} = -\sum_{\rho,k} \lambda_k^\rho n_k^\rho + \frac{1}{2} \sum_{\rho\sigma,kl} \tilde{v}_{kl}^{\rho\sigma} n_k^\rho n_l^\sigma, \\
\tilde{v}_{kl}^{\rho\sigma} = v_{kl}^{\rho\sigma} + h_{kl}^{\rho\sigma}.
\end{gathered} \tag{19}$$

Here, $\tilde{v}_{kl}^{\rho\sigma}$ can be regarded as the full effective interaction, which for simplicity is supposed to be pairwise, just as the "true" interaction $v_{kl}^{\rho\sigma}$ in Hamiltonian (4). The operator $\hat{E}^{in}_{pi,vj}$ in (18) (describing the part of the initial configurational energy that depends on occupations of sites i and j) can be expressed in terms of formal variational derivatives of Hamiltonian (3) with respect to n_{pi} and n_{vi}, $H^t_{pi} = \delta H^t/\delta n_{pi}$ and $H^t_{pi,vj} = \delta^2 H^t/\delta n_{pi}\delta n_{vj}$:

$$\hat{E}^{in}_{pi,vj} = n_{pi} H^t_{pi} + n_{vj} H^t_{vj} - n_{pi} n_{vj} H^t_{pi,vj}, \tag{20}$$

where the third term corresponds to the subtraction of the "double-counted" interaction between an atom p at site i and a vacancy v at site j.

The main idea of further manipulations (analogous to those made in [10, 11]) is to reduce the averages of complex operators in square brackets in (18) to

some simpler averages that have a clear physical meaning. For this, in the sums over all configurations $\{n_k^\rho\}$ in (18), we first perform summation over all possible occupations of only two sites, i and j, belonging to the ij bond under consideration. Due to the presence of the projection operator $n_i^p n_j^v$ in (18), the summation reduces to setting $n_i^q = \delta_{qp}$ and $n_j^\rho = \delta_{\rho v}$ in the n_i^q- and n_j^ρ-dependent exponential factor $\exp Y$ multiplied by this projection operator, where

$$Y = \beta(E_{pi,vj}^{in} - H_{eff}). \tag{21}$$

We note that the saddle-point energy $\hat{E}_{pi,vj}^{SP}$, according to its definition (10), does not contain occupation operators of sites i and j. The common factor $\omega_{pv}^{eff} \exp(\beta\Omega - \beta\hat{E}_{pi,vj}^{SP})$ is therefore skipped in Eqs. (23)–(26) for brevity.

In what follows, it is convenient to formally restore the summation over all occupation number sets $\{n_k^\rho\}$ in (18), including all values of n_i^ρ and n_j^σ. For this, we can introduce the operator $n_i^h n_j^h$ into the summand. Because this projection operator is nonzero only when all n_i^ρ and n_j^σ are zero, the summation with this factor over all possible occupations of sites i and j is equivalent to omitting all n_i^ρ- and n_j^σ-dependent terms in the exponential $\exp Y$. Therefore, the result of the summation can be written as

$$\sum_{n_i^\rho, n_j^\sigma} n_i^p n_j^v \exp Y = \\ = \sum_{n_i^\rho, n_j^\sigma} n_i^h n_j^h \exp\left(Y_{pi} + Y_{vj} + Y_{pi,vj} + Y\right), \tag{22}$$

where Y_{pi}, Y_{vj}, and $Y_{pi,vj}$ are variational derivatives of Y over the relevant occupation numbers: $Y_{pi} = \delta Y/\delta n_i^p$, etc. The first term in the exponent in Eq. (22) corresponds to the contribution to sum (22) of the term in Y linear in n_i^p but not in n_j^v, the second, to that of the term in Y linear in n_j^v but not in n_i^p, and the third, to that of the term in Y linear in both n_i^p and n_j^v.

We first consider the term with $p = \alpha$ in (22) and express all operators n_l^h in expression (20) for $E_{\alpha i,vj}^{in}$ in terms of the independent n_l^ρ using Eq. (1). After setting $n_i^\alpha = 1$ and $n_j^v = 1$ in that expression, the exponent Y in (21) takes the form

$$Y = \beta\left[\sum_{l\rho}\left(V_{il}^{\alpha\rho} - V_{il}^{\alpha h}\right) n_l^\rho + \sum_{l\rho}\left(V_{jl}^{v\rho} - V_{jl}^{vh}\right) n_l^\rho + \right. \\ \left. + \sum_l \left(V_{il}^{\alpha h} + V_{jl}^{vh}\right) - V_{ij}^{\alpha v} - H_{eff}\right]. \tag{23}$$

Using Eqs. (19) and (5), we can explicitly write relation (22) at $p = \alpha$ as

$$\sum_{n_i^\rho, n_j^\sigma} n_i^\alpha n_j^v \exp Y = \sum_{n_i^\rho, n_j^\sigma} n_i^h n_j^h \times \\ \times \exp\left\{\beta\left[\sum_{l\rho}(u_{il}^\rho + u_{jl}^\rho) n_l^\rho + \sum_l \left(V_{il}^{\alpha h} + V_{jl}^{vh}\right) - \right.\right. \\ \left.\left. - V_{ij}^{hh} - h_{ij}^{\alpha v} + \lambda_i^\alpha + \left(\lambda_j^v - \sum_{l\rho} h_{jl}^{v\rho} n_l^\rho\right) - H_{eff}\right]\right\} \tag{24}$$

where the quantity

$$u_{il}^\rho = V_{il}^{\rho h} - V_{il}^{hh} \tag{25}$$

can be called "the kinetic interaction" for a ρ-species atom (because it affects only mobilities but not thermodynamic properties [15]). We note that the vacancy concentration $c_i^v = \langle n_i^v \rangle$ in real substitution alloys is very small, and hence all n_l^v can be neglected in the statistical averages involved in Eqs. (18). Therefore, terms with n_l^ρ in (24) actually correspond to the minority atoms with $\rho = \beta \neq v$. In writing Eq. (24), we also used the above-mentioned argument that for the usual conditions of phase transitions, significant renormalizations $h_{ij}^{v\alpha}$ can be expected only for the vacancy–atom interactions, while for the interactions between different atoms, the analogous renormalizations $h_{ij}^{\alpha\beta}$ are not essential.

In the case $p = h$, Eq. (22) is simplified because the operator Y in (21) depends only on the independent operators n_j^ρ but not on n_i^h. Therefore, the terms Y_{hi} and $Y_{hi,vj}$ in (22) are absent and the exponent reduces to $(Y_{vj} + Y)$. Making the same manipulations as above, we then obtain instead of (24),

$$\sum_{n_i^\rho, n_j^\sigma} n_i^h n_j^v \exp Y = \sum_{n_i^\rho, n_j^\sigma} n_i^h n_j^h \times \\ \times \exp\left\{\beta\left[\sum_{l\beta}(u_{il}^\beta + u_{jl}^\beta) n_l^\beta + \sum_l \left(V_{il}^{hh} + V_{jl}^{vh}\right) - V_{ij}^{hh} + \right.\right. \\ \left.\left. + \left(\lambda_j^v - \sum_{l\beta} h_{jl}^{v\beta} n_l^\beta\right) - H_{eff}\right)\right]\right\}. \tag{26}$$

Substituting relations (24) and (26) in (18), we can express the derivatives dc_i^ρ/dt via some statistical averages. In writing these averages, we can take into account that the interaction renormalizations $\hat{h}_{int}$ in (12) are present only for the vacancy–atom terms $h_{ij}^{v\beta} n_i^v n_j^\beta$, which include the vacancy occupation operators n_i^v and

can therefore be neglected. Hence, quasi-equilibrium distribution (15) can be used in calculations of these averages. To simplify formulas, in treating the interaction renormalization terms $h_{jl}^{v\beta}n_l^\beta$ in Eqs. (24) and (26), we use the mean field approximation (MFA), replacing each operator n_l^β in these averages by its mean value c_l^β. Therefore, each term $h_{jl}^{v\beta}n_l^\beta$ is replaced by $h_{jl}^{v\beta}c_l^\beta$, which corresponds to replacing the vacancy site chemical potential λ_i^v by its "renormalized" value $\tilde\lambda_i^v$:

$$\left(\lambda_i^v - \sum_{l\beta} h_{jl}^{v\beta}n_l^\beta\right) \to \tilde\lambda_i^v = \left(\lambda_i^v - \sum_{l\beta} h_{jl}^{v\beta}c_l^\beta\right). \quad (27)$$

We show in Sec. 2.2 that for c_l^β values close to unity, when the interaction renormalization effects can be expected to be most significant, approximation (27) becomes exact. Hence, we can expect it to be sufficiently accurate at all c_l^β. We also note that a similar MFA treatment of interaction renormalization effects have been used in [11, 13], where the comparison of MFA and kinetic Monte Carlo results have shown that the MFA accuracy is sufficient for treatments of renormalization effects.

Using relations (24)–(27), we can write Eqs. (18) in the concise form

$$\frac{dc_i^\alpha}{dt} = \sum_{j(i)} \gamma_{\alpha v} b_{ij}^\alpha (\xi_i^v \eta_j^\alpha - \xi_j^v \eta_i^\alpha),$$

$$\frac{dc_i^v}{dt} = \quad (28)$$

$$= \sum_{j(i)} \left[\xi_j^v \left(\gamma_{hv} b_{ij}^h + \sum_\beta \gamma_{\beta v} b_{ij}^\beta \eta_i^\beta\right) - \{i \to j\}\right],$$

which is called the "quasi-equilibrium" kinetic equations (QKE) in what follows. The term γ_{pv} in these equations (where p is α or h, i. e., denotes a minority or a host atom) is the effective exchange rate $p \rightleftharpoons$v for a pure host metal. This term can be written in a form similar to Eq. (7),

$$\gamma_{pv} = \omega_{pv}^{eff} \exp(-\beta E_{ac}^{pv}), \quad (29)$$

where ω_{pv}^{eff} is the same as in (8), while E_{ac}^{pv} is the effective activation energy, which is expressed in terms of the saddle-point energies E_h^p in (11) and the interactions $V_{ij}^{p'q'}$ and $h_{ij}^{\alpha v}$ in (3) and (19) as

$$E_{ac}^{\alpha v} = E_h^p - \sum_j (V_{ij}^{ph} + V_{ij}^{vh}) + V_{nn}^{hh} + h_{ij}^{\alpha v}, \quad (30)$$

$$E_{ac}^{hv} = E_h^h - \sum_j (V_{ij}^{hh} + V_{ij}^{vh}) + V_{nn}^{hh}, \quad (31)$$

where nn means "nearest neighbors". Comparing these expressions with the analogous activation energies $E_{ac,MC}^{pv}$ used in the kinetic Monte Carlo approach [14] and given by Eq. (2.5) in [26], we find

$$E_{ac}^{\alpha v} = E_{ac,MC}^{\alpha v} + \tilde v_{nn}^{\alpha v}, \quad E_{ac}^{hv} = E_{ac,MC}^{hv}, \quad (32)$$

where $\tilde v^{\alpha v}$ is the same as in (19). The difference between $E_{ac}^{\alpha v}$ and $E_{ac,MC}^{\alpha v}$ arises because transition probability (7) in the statistically averaged QKE (28) is averaged over distribution (12). For the intersite exchange $\alpha i \rightleftharpoons vj$, this leads to an extra Gibbs factor $\exp(-\beta\tilde v_{ij}^{\alpha v})$ in the averaged probability, with $\tilde v_{ij}^{\alpha v}$ defined in (19).

We note in this connection that in their study of diffusion in dilute Fe–Cu alloys [14] with the correlation effects for this vacancy-mediated diffusion thoroughly taken into account [27], SF obtained the value $(E_{ac}^{\mathrm{Cu}v})_{eff} \approx 0.47$ eV for the effective activation energy of a copper atom [26, 28]. This is very close to the value $E_{ac}^{\mathrm{Cu}v} = 0.44$ eV that follows from Eq. (30) at $h_{ij}^{\mathrm{Cu}v} = 0$ after the substitution of couplings V_{ij}^{pq} used by SF. This may imply that for the diffusion in dilute Fe–Cu alloys, our statistical averaging with quasi-equilibrium Gibbs distribution (15) can rather accurately describe the relevant correlation effects [27], while the interaction renormalization effects are not very significant for this diffusion.

The quantities b_{ij}^p in (28) (to be called "correlators") are certain averages of site occupations and describe the influence of minority atoms in the vicinity of the bond ij on the $pi \rightleftharpoons vj$ jump probability:

$$b_{ij}^p = \left\langle n_i^h n_j^h \exp\left[\sum_{\alpha l} \beta(u_{il}^\alpha + u_{jl}^\alpha) n_l^\alpha - \right.\right.$$

$$\left.\left. - \sum_{\alpha,\, l=l_{nn}^{ij}} \beta\Delta_\alpha^p n_l^\alpha\right]\right\rangle, \quad (33)$$

where Δ_α^p is the same as in (11) and u_{il}^α is the same as in (24)–(26).

Finally, the quantities ξ_i^v and η_i^α in (28) can be respectively called the "site thermodynamic activities" for vacancies and α-species atoms because they are related to the site chemical potentials λ_i^α in (15) and the renormalized site chemical potential $\tilde\lambda_i^v$ in (27) as

$$\xi_i^v = \exp(\beta\tilde\lambda_i^v), \quad \eta_i^\alpha = \exp(\beta\lambda_i^\alpha) \quad (34)$$

(which is similar to the relations between conventional thermodynamic activities and chemical potentials).

2.2. Calculations of site chemical potentials λ_i^ρ and correlators b_{ij}^p

To find explicit expressions for the site chemical potentials $\lambda_i^\rho = \lambda_i^\rho(c_j)$ determined by Eqs. (17) and for the correlators $b_{ij}^p = b_{ij}^p(c_k)$ determined by Eqs. (33), we should use some approximate method of statistical physics, such as the MFA or cluster methods [12]. As discussed in detail in [15, 21, 29], using the MFA for calculations of chemical potentials λ_i^ρ in real alloys often leads to large errors, while the pair cluster approximation (PCA) usually combines simplicity of calculations with high accuracy, particularly for dilute alloys. As an illustration (used also below for interstitial alloys), we present the PCA expressions for λ_i^ρ in a binary A–B–v alloy with host atoms $h = A$ and minority atoms $\alpha = B$ (omitting the index B at $\lambda_i^{\mathrm{B}} = \lambda_i$ and $c_i^{\mathrm{B}} = c_i$ for brevity):

$$\lambda_i = T\left[\ln(c_i/c_i^h) + \sum_{j\neq i}\ln(1-g_{ij}c_j)\right], \tag{35}$$

$$\lambda_i^v = T\left[\ln(c_i^v/c_i^h) - \sum_{j\neq i}\ln(1+g_{ij}^v c_j)\right]. \tag{36}$$

Here, the function g_{ij} or g_{ij}^v is expressed in terms of the Mayer function $f_{ij} = [\exp(-\beta v_{ij}) - 1]$ or $f_{ij}^v = [\exp(-\beta v_{ij}^{v\mathrm{B}}) - 1]$ for the potential $v_{ij} \equiv v_{ij}^{\mathrm{BB}}$ or $v_{ij}^{v\mathrm{B}}$ defined in (5) as

$$\begin{aligned} g_{ij} &= 2f_{ij}/[R_{ij} + 1 + f_{ij}(c_i + c_j)],\\ g_{ij}^v &= 2f_{ij}^v/[R_{ij} + 1 + f_{ij}(c_i - c_j)],\\ R_{ij} &= \left\{[1+(c_i+c_j)f_{ij}]^2 - 4c_ic_jf_{ij}(f_{ij}+1)\right\}^{1/2}. \end{aligned} \tag{37}$$

For a multicomponent alloy A–B_1–... B_m–v, the PCA methods of calculations of site chemical potentials λ_i^ρ are described in [21].

In calculating the correlators b_{ij}^p in (33), for simplicity, we first consider the case of configuration-independent saddle-point energies when the differences $\hat{\Delta}_\alpha^p$ and Δ_α^p in Eqs. (10), (11) and (33) are zero and the correlators $b_{ij}^p = b_{ij}$ are independent of the kind of a jumping atom p. Using Eqs. (2) and the identity

$$\exp(xn_l^\alpha) = 1 + n_l^\alpha f(x), \quad f(x) = e^x - 1, \tag{38}$$

which follows from (2), we can rewrite Eq. (33) as

$$\begin{aligned} b_{ij} &= \left\langle n_i^h n_j^h \prod_{l=1}^{k_t}(1 + \sum_\alpha f_l^\alpha n_l^\alpha)\right\rangle = \\ &= \sum_{k=0}^{k_t}\sum_{l_1\neq\ldots l_k}\sum_{\alpha_1\ldots\alpha_k}\left\langle n_i^h n_j^h n_{l_1}^{\alpha_1}\ldots n_{l_k}^{\alpha_k}\right\rangle \times \\ &\qquad \times f_{l_1}^{\alpha_1}\ldots f_{l_k}^{\alpha_k}, \end{aligned} \tag{39}$$

where we set

$$f_l^\alpha = f(\beta u_{il}^\alpha + \beta u_{jl}^\alpha) \tag{40}$$

with $f(x)$ defined in (38), and k_t is the total number of sites with nonzero values of potentials $u_{il}^\alpha + u_{jl}^\alpha$. For example, for the nearest-neighbor or next-to-nearest-neighbor interaction models in a BCC lattice [15], $k_t = 14$ or $k_t = 20$.

In finding the averages in (39), we recall that the functions f_l^α in Eqs. (39) and (40) are typically rather large for real alloys. For example, for the BCC Fe–Cu-v alloys considered in [15], $f(\beta u_1) \sim 5$ and $f(\beta u_2) \sim 1$ (where the interactions u_1 and u_2 correspond to the nearest and next-to-nearest neighbors). Hence, the leading contributions to sum (39) come from averages of products of many different operators n_l^α corresponding to well-separated and weakly correlated sites l. In particular, for the BCC lattice, these products (even for the nearest-neighbor interaction model) include terms with the neighbors from first to tenth, most often third and fourth. Correlations of occupations of so distant sites should typically be weak. Therefore, using the simple MFA that neglects such correlations should generally be admissible in calculations of averages (39), in contrast to the calculations of chemical potentials λ_i mentioned above.

In the MFA, each operator n_l^p in Eq. (39) is replaced by its mean value c_l^p. Hence, the correlator b_{ij} can be explicitly written as

$$\begin{aligned} b_{ij} &= c_i^h c_j^h \prod_{l=1}^{k_t}\left(1 + \sum_\alpha c_l^\alpha f_l^\alpha\right) = \\ &= c_i^h c_j^h \exp\left[\sum_{l=1}^{k_t}\ln\left(1 + \sum_\alpha f_l^\alpha c_l^\alpha\right)\right]. \end{aligned} \tag{41}$$

When the differences Δ_α^p in Eqs. (11) and (33) are nonzero, the correlator b_{ij}^p in Eq. (33) can be calculated in the same way as b_{ij} in (39)–(41). The difference arises only for sites $l = l_{nn}^{ij}$ adjacent to the ij bond, for which the factor f_l^α defined in Eq. (40) is replaced by an analogous factor $f_{l\Delta}^{\alpha p}$ defined as

$$f_{l\Delta}^{\alpha p} = f(\beta u_{il}^\alpha + \beta u_{jl}^\alpha - \beta\Delta_{\alpha l}^p \delta_{l,l_{nn}^{ij}}), \tag{42}$$

where $\Delta^p_{\alpha l} = \Delta^p_\alpha \delta_{l,l^{ij}_{nn}}$ and $\delta_{l,l^{ij}_{nn}}$ is unity when $l = l^{ij}_{nn}$ and zero when $l \neq l^{ij}_{nn}$. Therefore, the correlator b^p_{ij} is given by Eq. (41) with each f^α_l replaced by $f^{\alpha p}_{l\Delta}$:

$$b^p_{ij} = c^h_i c^h_j \exp\left[\sum_{l=1}^{k_t} \ln\left(1 + \sum_\alpha f^{\alpha p}_{l\Delta} c^\alpha_l\right)\right]. \qquad (43)$$

We finally remark about the MFA-type approximation in (27) used in the derivation of QKE (28). If we do not use this approximation, then Eqs. (28), instead of the correlators b^p_{ij} in (43), include similar correlators $\tilde{b}^p_{ij}$ differing from b^p_{ij} by the presence of additional interaction renormalization terms $\beta h^{v\beta}_{jl} n^\alpha_l$ in the exponents:

$$\tilde{b}^p_{ij} = c^h_i c^h_j \exp \sum_{l=1}^{k_t} \ln\left\{1 + \sum_\alpha \left[\exp\left(\beta u^\alpha_{il} + \beta u^\alpha_{jl} - \right.\right.\right.$$
$$\left.\left.\left. - \beta\Delta^p_{\alpha l} - \beta h^{v\alpha}_{jl}\right) - 1\right] c^\alpha_l\right\}, \qquad (44)$$

where we write the function $f(x)$ defined in (38) explicitly. For the diffusional transformations under consideration, the interaction renormalization effects seem to be most significant in those spatial regions where the local concentration c^α_l is close to unity. This is illustrated by the case of precipitation in Fe–Cu alloys, where these effects arise due to the strong trapping of vacancies by the Cu-based precipitates for which c^{Cu}_l is close to unity [15]. For such c^α_l, the argument of the logarithm in (44) reduces to a single exponential, and relation (27) becomes exact. We also note that for simulations of diffusional transformations based on Eq. (28), the details of vacancy distributions are actually insignificant due to the "adiabaticity principle" and the "time rescaling" procedure discussed in Sec. 2.3. Therefore, approximation (27) appears to be sufficient for the use in such simulations.

2.3. Reducing kinetic equations (28) to equations for some direct exchange model

Quasi-equilibrium kinetic equations (28) can be used for modeling most different phase transformations, in particular, processes of precipitation, which attract great attention in connection with numerous applications [30–32]. However, in their original form (28), these equations are not suitable for using in computer simulations due to very small values of vacancy concentration c_v in real alloys. Because atomic exchanges $pi \leftrightharpoons vj$ occur only with a vacancy, this smallness leads to a great difference in the relaxation times τ between atoms α and vacancies v: $\tau_\alpha \sim \tau_v/c_v \gg \tau_v$. This is illustrated by the presence of vacancy activities $\xi^v_i = \exp(\beta\tilde{\lambda}^v_i)$ in the right-hand side of QKE (28). This activity is proportional to the vacancy concentration c^v_i, which is a general relation of thermodynamics of dilute solutions illustrated by Eq. (36). Therefore, the time derivatives of mean occupations are proportional to the local vacancy concentration, c^v_i or c^v_j. This is natural for the vacancy-mediated kinetics and leads to the strong inequality between τ_α and τ_v mentioned above. Therefore, the type of temporal evolution for atoms and vacancies is quite different, which makes the direct numerical solution of Eqs. (28) for $c^v_i(t)$ and $c^\alpha_i(t)$ unsuitable and time consuming.

At the same time, the inequality $\tau_\alpha \gg \tau_v$ allows using the "adiabatic" approach encountered in many fields of physics, including the well-known Born–Oppenheimer approach in the quantum mechanical description of the motion of atoms in molecules and solids. In this approach, the effective driving force for a slow motion is obtained by its averaging over a rapid motion. Therefore, to fully describe the slow motion, only a few averaged characteristics of the rapid motion are needed. In quantum mechanics, this is the appropriate electronic energy ("electronic term") calculated at fixed positions $\mathbf{R}_i$ of atoms. In our problem, this means that at a given atomic distribution $\{c^\alpha_i\}$, the local vacancy concentration c^v_i adiabatically fast (i. e., in a time $\tau_v \sim c_v\tau_\alpha \ll \tau_\alpha$) reaches its "quasi-equilibrium" value $c^v_i\{c^\alpha_i\}$ for which the right-hand side of the second equation in (28) vanishes. Therefore, discarding small corrections of the relative order $c^v_i \ll 1$, we can approximate this equation by its adiabatic version

$$0 = \sum_{j(i)} \left[\xi^v_j \left(\gamma_{hv} b^h_{ij} + \sum_\alpha \gamma_{\alpha v} b^\alpha_{ij} \eta^\alpha_i\right) - \right.$$
$$\left. - \{i \to j\}\right], \qquad (45)$$

which can be called "the adiabaticity equation" for the vacancy activity ξ^v_i. Solving this linear equation for ξ^v_i, we can, in principle, express it in terms of c^α_j. Substituting these $\xi^v_i(c^\alpha_j)$ in the first equation in (28) then yields the QKE for some equivalent direct-atomic-exchange (DAE) model.

To illustrate these considerations, we first consider models with configuration-independent saddle-point energies. For such models, the parameters Δ^p_ρ in (11) are zero, the correlators $b^p_{ij} = b_{ij}$ are independent of the species p of the jumping atom, and adiabaticity equation (45) takes the simple form

$$\sum_{j(i)} b_{ij}\,\xi_i^v\,\xi_j^v\left[\left(\gamma_{hv}+\sum_\alpha \gamma_{\alpha v}\eta_i^\alpha\right)\Big/\xi_i^v - \{i\to j\}\right] = 0. \quad (46)$$

If we let $1/\nu_i$ denote the first term in the square brackets, then the difference in these brackets takes the form $\nu_i^{-1}-\nu_j^{-1}$. Hence, a solution of Eqs. (46) is given by ν_i being a constant independent of the site number i (although possibly depending on time as well as on temperature and other external parameters):

$$\nu_i = \xi_i^v\Big/\left(\gamma_{hv}+\sum_\alpha \gamma_{\alpha v}\eta_i^\alpha\right) = \nu(t). \quad (47)$$

Relation (47) determines the above "quasi-equilibrium" vacancy distribution $c_i^v\{c_i^\alpha\}$, which adiabatically fast follows the atomic distribution $\{c_i^\alpha\}$. Substituting it in the first equation in (28), we obtain an explicit kinetic equation for atomic distributions $\{c_i^\alpha\}$ for which the evolution of the vacancy distribution is characterized by a single parameter $\nu(t)$ being a "spatially self-averaged" quantity:

$$\frac{dc_i^\alpha}{dt} = \sum_{j(i)} b_{ij}\nu(t)\left[\gamma_{\alpha v}\gamma_{hv}\left(\eta_j^\alpha-\eta_i^\alpha\right) + \sum_\beta \gamma_{\alpha v}\gamma_{\beta v}\left(\eta_j^\alpha\eta_i^\beta-\eta_i^\alpha\eta_j^\beta\right)\right]. \quad (48)$$

Equations (48) can also be rewritten in the form used in DAE models [12]:

$$\frac{dc_i^\alpha}{dt} = \sum_{j(i)} M_{ij}^{\alpha h}\,2\,\mathrm{sh}\left[\frac{\beta}{2}(\lambda_j^\alpha-\lambda_i^\alpha)\right] + \sum_{j(i),\,\beta} M_{ij}^{\alpha\beta}\,2\,\mathrm{sh}\left[\frac{\beta}{2}(\lambda_j^\alpha+\lambda_i^\beta-\lambda_i^\alpha-\lambda_j^\beta)\right], \quad (49)$$

where the generalized mobilities M_{ij}^{pq} describing the intersite exchanges $\alpha \leftrightharpoons h$ and $\alpha \leftrightharpoons \beta$ are given by

$$M_{ij}^{\alpha h} = \gamma_{\alpha v}\gamma_{hv}\nu(t)\,b_{ij}\exp\left[\beta(\lambda_i^\alpha+\lambda_j^\alpha)/2\right], \quad (50)$$

$$M_{ij}^{\alpha\beta} = \gamma_{\alpha v}\gamma_{\beta v}\nu(t)\,b_{ij}\times \exp\left[\beta(\lambda_i^\alpha+\lambda_j^\alpha+\lambda_i^\beta+\lambda_j^\beta)/2\right]. \quad (51)$$

Comparing these expressions with expression (32) in [10], which describes the mobility M_{ij}^{pq} in an alloy with the nearest-neighbor direct-exchange rate $\gamma_{ij}^{pq}=\gamma_{pq}$, we see that Eqs. (50) and (51) correspond to a DAE model with the effective direct exchange rates

$$\gamma_{\alpha h}^{eff} = \gamma_{\alpha v}\gamma_{hv}\nu(t), \quad \gamma_{\alpha\beta}^{eff} = \gamma_{\alpha v}\gamma_{\beta v}\nu(t). \quad (52)$$

Because $\nu(t)$ in (47) is proportional to c_i^v, the effective DAE rates in (52) are by a factor c_v smaller than the vacancy exchange rates γ_{pv}, in accordance with the above-discussed adiabaticity relations.

For more realistic models with configuration-dependent saddle-point energies, the basic adiabaticity equation (45) for vacancy activities ξ_i^v cannot be solved analytically in general, and hence either numerical or some approximate analytic methods should be used. For the first-principle model of Fe–Cu–v alloys developed in [14], such an approximate treatments in [15] have shown that equivalence relations (48)–(52) usually preserve their form, but the correlator b_{ij} is replaced by some other quantity, b_{ij}^{Cu} or b_{ij}^{Fe}. Physically, the possibility to reduce the vacancy-mediated kinetics to the equivalent direct atomic exchange kinetics is related with the above-mentioned fact that in the course of evolution of an alloy, the distribution of vacancies follows that of the main components adiabatically fast. Therefore, it can be assumed that this equivalence is actually a general feature of vacancy-mediated kinetics, while for more general models, the correlators b_{ij} in (50) can be replaced by some other expressions with similar properties.

The function $\nu(t)$ in Eq. (52) determines the rescaling of time between the initial vacancy-mediated exchange model and the equivalent DAE model Eqs. (48)–(52). Temporal evolution of this DAE model is actually described by the dimensionless "reduced time" t_r related to the real time t by the differential or integral relations

$$dt_r = \gamma_{\alpha h}^{eff}\,dt = \gamma_{\alpha v}\gamma_{hv}\nu(t)\,dt, \quad t_r = \int_0^t \gamma_{\alpha h}^{eff}(t')\,dt', \quad t = \int_0^{t_r} dt'_r\,\tau_{\alpha h}^{eff}(t'_r), \quad (53)$$

where $\tau_{\alpha h}^{eff} = 1/\gamma_{\alpha h}^{eff}$ has the meaning of the mean time of an atomic exchange $\alpha \leftrightharpoons h$ and t_r has the meaning of an effective number of such atomic exchanges.

The form of the function $t(t_r)$ in (53) depends on the boundary conditions for vacancies adopted in simulations. In particular, if we adopt the "vacancy conservation" model for which the interaction renormalization effects can be expected to be insignificant, then we can use Eqs. (47) and (36) to express the local vacancy concentration c_i^v via $\nu(t)$ and $c_i^\alpha(t_r)$. Then the vacancy

conservation condition $\sum_i c_i^v(t,t_r) = N_v = \text{const}$ can be used to explicitly find the dependence $t(t_r)$. However, in view of a possible creation of vacancies at various lattice defects (grain boundaries, dislocations, etc.), the kinetic Monte Carlo (KMC) simulations [14, 26] taking into account such precesses appear to be more realistic. Then the dependences $t(t_r)$ can be found by comparing the results of the DAE-based simulations described above with the appropriate KMC results, as was illustrated in [15]; these dependences seem to be rather simple and universal. In more detail, applications of Eqs. (48)–(53) to studies of precipitation in specific alloys will be described elsewhere.

3. EQUATIONS FOR DIFFUSION OF INTERSTITIAL ATOMS IN INTERSTITIAL ALLOYS

In binary interstitial alloys Me–X, where X is an interstitial atom, and in iron–carbon steels in particular, diffusion of atoms X is realized via thermo-activated jumps of these atoms between their interstitial sites ("pores"). Therefore, this diffusion can be described by the general equations in Sec. 2 for a particular case of a substitution binary alloy X–v that consists of atoms $\alpha = \text{X}$ and vacancies v in the crystal lattice of pores, with the "host" atoms h being vacancies v. The total configurational Hamiltonian (3) here includes X–X interactions between atoms X, but not X–v and v–v interactions. Therefore, only V_{ij}^{XX} terms are nonzero in formulas (3)–(5):

$$V_{ij}^{\alpha\alpha} = V_{ij}^{\text{XX}} \neq 0, \quad V_{ij}^{\alpha h} = V_{ij}^{hh} = 0. \tag{54}$$

The only meaningful index $\alpha = \text{X}$ is usually omitted below, for example, $c_i^{\text{X}} = c_i$ and $V_{ij}^{\text{XX}} = v_{ij}$, and hence the effective Hamiltonian (19) takes the form

$$\begin{aligned} H_{eff} &= -\sum_i \lambda_i n_i + H_{int}, \\ H_{int} &= \frac{1}{2}\sum_{ij} v_{ij} n_i n_j. \end{aligned} \tag{55}$$

The mean occupation $c_i = \langle n_i \rangle$ of a pore i by an atom X is related to the local chemical concentration x_i by the relation depending on the geometry of pores [2], e. g., $c = x/(1-x)$ for a uniform austenite structure MeX_c with the FCC lattice of octo-pores.

An important principal feature whereby the diffusional kinetics in the interstitial Me–X (i. e., substitution X–v) alloys differs from that in the substituton A–B–v alloys is the validity for Me–X alloys of relation (14), that is, the absence of the interaction renormalization effects. This follows, first, from the physical considerations presented after Eqs. (14) and (15) and, second, from the thorough analysis of interaction renormalization effects for A–B–v alloys in [11, 13]. It was found there that these effects are described by terms antisymmetric with respect to the transposition of A and B atoms, $h_{ij}^{\text{AB}} - h_{ij}^{\text{BA}}$, which vanish in a binary X–v alloy, where A = B = X. Therefore, the diffusional kinetics in Me–X alloys can be described by quasi-equilibrium relations (14) and (15).

For a uniform Me–X alloy, the site chemical potential $\lambda_i = \lambda$ in (55) coincides with the thermodynamic chemical potential μ_{X}, in contrast to the case of substitution alloys, where the analogous quantity λ_α, as mentioned in Sec. 2.1, is equal to the difference $\mu_\alpha - \mu_h$. To show this, we generalize Eqs. (21)–(24) and (40)–(43) in Ref. [21] to the case of interstitial alloys Me–X. Quasi-equilibrium Gibbs distribution (15) and the generalized grand canonical potential Ω_g for effective Hamiltonian (55) are given by

$$P = \exp\left[\beta(\Omega_g + \sum_i \lambda_i n_i - H_{int})\right], \tag{56}$$

$$\Omega_g = -T \ln \sum_{\{n_{\alpha i}\}} \exp\left[\beta\left(\sum_i \lambda_i n_i - H_{int}\right)\right], \tag{57}$$

while the mean occupation c_i is related to $\Omega_g\{\lambda_i\}$ by the formula obtained by differentiating equality (57):

$$c_i = \langle n_i \rangle = -\partial\Omega_g/\partial\lambda_i. \tag{58}$$

Therefore, if we define the generalized free energy F by the equality

$$F = \Omega_g + \sum_i \lambda_i c_i \tag{59}$$

then the site chemical potential λ_i is related to F by the relations generalizing those for a uniform alloy:

$$\lambda_i = \partial F/\partial c_i. \tag{60}$$

To relate λ_i and Ω_g in Eqs. (56)–(60) to the thermodynamic chemical potentials, we consider the case of a uniform alloy Me–X, where c_i and λ_i in Eqs. (56)–(60) are independent of i: $c_i = c$ and $\lambda_i = \lambda$. For definiteness, we discuss the austenite structure for which the total number of interstitial sites (octo-pores) is equal to the total number N_{Me} of Me atoms. Then instead of the total thermodynamic potentials Ω_g and F, it is convenient to consider the analogous quantities per one Me atom, Ω and f:

$$\begin{gathered} \Omega = \Omega_g/N_{\text{Me}}, \quad f = F/N_{\text{Me}} = \Omega + \lambda c, \\ c = N_{\text{X}}/N_{\text{Me}}. \end{gathered} \tag{61}$$

Here, $N_{\rm X}$ is the total number of atoms X, and hence c is the mean occupation of an interstitial site, and, according to Eq. (60),

$$\lambda = \partial f/\partial c. \tag{62}$$

The quantities Ω and λ in Eqs. (61) and (62) are simply related to the partial chemical potentials $\mu_{\rm X}$ and $\mu_{\rm Me}$ defined by the thermodynamic relations

$$\mu_{\rm X} = \partial F/\partial N_{\rm X}, \quad \mu_{\rm Me} = \partial F/\partial N_{\rm Me}. \tag{63}$$

Substituting relations (61) for c and $F = N_{\rm Me} f(c)$ in Eqs. (63) and taking Eq. (62) into account, we obtain

$$\lambda = \mu_{\rm X}, \quad \Omega = \mu_{\rm Me}. \tag{64}$$

Hence, the quantities λ and Ω in Eqs. (61) and (62) have the respective meaning of the chemical potentials of X atoms and Me atoms.

Kinetic equation describing diffusion of atoms X in an interstitial alloy Me–X (treated as a binary substitution alloy X-v) can be derived analogously to Eqs. (28) with the simplifications implied by Eqs. (54) and (55). Taking into account Eqs. (34), (27), (54), (55) and relations $v = h$, $\lambda_i^v = \lambda_i^h = 0$, this equation can also be obtained simply putting $\xi_i^v = 1$ in the first equation (28):

$$\frac{dc_i}{dt} = \sum_{j(i)} \gamma_{ij} b_{ij}^{\rm X} \left[\exp(\beta\lambda_j) - \exp(\beta\lambda_i)\right]. \tag{65}$$

The jump probability γ_{ij} and the correlator $b_{ij}^{\rm X}$ in (65) are defined by relations analogous to (29) and (33):

$$\gamma_{ij} = \omega_{ij}^{eff} \exp(-\beta E_{ac}^{ij}), \tag{66}$$

$$b_{ij}^{\rm X} = \left\langle (1-n_i)(1-n_j) \exp\left(-\beta \sum_k \Delta_k^{ij} n_k\right)\right\rangle. \tag{67}$$

The pre-exponent ω_{ij}^{eff} in (66) is determined by Eq. (8) with the replacement $p \to {\rm X}$, and the activation energy E_{ac}^{ij} reduces to the term $E_h^p = E_v^{\rm X}$ in (10), unlike the more complex expression (31) in a substitutional alloy. The index "ij" at the quantities ω_{ij}^{eff} and E_{ac}^{ij} in (66) allows for a possible nonuniformity of an alloy; for a uniform alloy, this index can be omitted. The quantity Δ_k^{ij} in (67) is an analogue of Δ_{ij}^p in Eqs. (10) and (11); it describes the change of the saddle-point energy $E_{{\rm X}i,vj}^{SP}$ for an inter-site X-atom jump $i \to j$ due to the presence of another atom X at site k.

Kinetic equation (65) can also be written in a form analogous to Eq. (49):

$$\frac{dc_i}{dt} = \sum_{j(i)} 2M_{ij} \operatorname{sh}\left[\frac{\beta}{2}(\lambda_j - \lambda_i)\right], \tag{68}$$

where the generalized mobility M_{ij}, according to (65), is determined by the relation

$$M_{ij} = \gamma_{ij} b_{ij}^{\rm X} \exp\left[\frac{\beta}{2}(\lambda_i + \lambda_j)\right]. \tag{69}$$

In usual diffusion problems, the spatial dependence of the functions $c_i = c(\mathbf{r}_i)$, $\lambda_i = \lambda(c_i)$, and $b_{ij}^{\rm X} = b_{ij}^{\rm X}(c_i, c_j)$ in Eqs. (65)–(69) is supposed to be smooth. Therefore, variations of these functions under the replacements $c_i \to c_j$ (or $\mathbf{r}_i \to \mathbf{r}_j = \mathbf{r}_i + \mathbf{r}_{ji}$, where $\mathbf{r}_{ji} = \mathbf{r}_j - \mathbf{r}_i$ is the interpore distance) are small. Then kinetic equation (65) or (68) can be expanded in powers of $\mathbf{r}_{ji}\nabla c$. This yields a continuous version of this kinetic equation in the form of a "continuity equation" for the flux $\mathbf{j}$ of atoms X:

$$\frac{\partial c}{\partial t} + \operatorname{div}\mathbf{j} = 0, \quad j_\alpha = -\sum_\nu D_{\alpha\nu}(c)\nabla_\nu c. \tag{70}$$

Here, α and ν are Cartesian indices and the diffusivity $D_{\alpha\nu}$ is determined by the expression

$$D_{\alpha\nu}(c) = \Gamma_{\alpha\nu} b_{\rm X} \frac{\partial a_{\rm X}}{\partial c}, \tag{71}$$

$$\Gamma_{\alpha\nu} = \frac{1}{2}\sum_{j(i)} \gamma_{ij} r_{ij}^\alpha r_{ij}^\nu, \tag{72}$$

where $a_{\rm X} = a_{\rm X}(c,T) = \exp[\beta\lambda(c,T)]$ is the thermodynamic activity of X atoms and $b_{\rm X} = b_{\rm X}(c,T)$ is the correlator $b_{ij}^{\rm X}$ in Eq. (67) at $c_i = c_j = c$.

The site chemical potential λ_i in a binary alloy can be written as

$$\lambda_i = \lambda_i^{id} + \lambda_i^{int}, \tag{73}$$

where $\lambda_i^{id} = T\ln[c_i/(1-c_i)]$ corresponds to the ideal solution and λ_i^{int} describes interaction effects, see, e. g., (35). Therefore, for the ideal solution for which both λ_i^{int} in (73) and Δ_l^{ij} in (67) are zero, we have $a_{\rm X} = c/(1+c)$, $b_{\rm X} = (1-c)^2$, and $b_{\rm X}\partial a_{\rm X}/\partial c = 1$ and Eq. (70) becomes the simple linear diffusion equation

$$\frac{\partial c}{\partial t} = \sum_{\alpha\nu} D_{\alpha\nu}^{id} \nabla_{\alpha\nu}^2 c \tag{74}$$

with the concentration-independent diffusivity $D_{\alpha\nu}^{id}$ equal to $\Gamma_{\alpha\nu}$ in (72). However, when X–X interactions v_{ij} and Δ_l^{ij} are significant, kinetic equation (70) is nonlinear and the diffusivity $\mathbf{D}$ in (71) should vary with the local concentration $c = c^{\rm X}(\mathbf{r})$.

For a uniform cubic alloy, such as austenite, the tensor $\Gamma_{\alpha\nu}$ reduces to a scalar $\delta_{\alpha\nu}\gamma a^2$, where γ is given by

Eq. (66) (with the index ij omitted) and a is the FCC iron (γ-iron) lattice constant, whence $D_{\alpha\nu} = \delta_{\alpha\nu} D$. According to (71), the diffusivity D can then be written as

$$D = \gamma a^2 b_{\rm X} \frac{\partial a_{\rm X}}{\partial c}, \tag{75}$$

where γ is defined by Eqs. (66) and (8) with the appropriate change of indices:

$$\gamma = \omega_{\rm X}^{eff} \exp(-\beta E_{ac}), \quad \omega_{\rm X}^{eff} = \omega_{\rm X} \exp\left(\Delta S_{\rm X}^{SP}\right). \tag{76}$$

For a uniform alloy with $c_i = c$, PCA expression (35) for the local chemical potential $\lambda(c)$ is simplified [29]:

$$\begin{gathered} \lambda(c,T) = T \sum_n z_n \ln(1 - g_n c), \\ g_n = 2f_n/(R_n + 1 + 2cf_n), \\ f_n = \exp(-\beta v_n) - 1, \quad R_n = [1 + 4c(1-c)f_n]^{1/2}, \end{gathered} \tag{77}$$

where z_n is the coordination number and v_n is the configurational interaction for the nth coordination sphere. In the case of weak interaction, $\beta v_n \ll 1$, Eq. (77) reduces to the MFA expression $\lambda^{\rm MFA} = \left(\sum_n z_n v_n\right) c$. But for the realistic values of the interactions v_n, such as those in Table 1, using the MFA can lead to significant errors [29].

The correlator $b_{\rm X}(c,T)$ for a uniform alloy, according to Eqs. (67) and (44), can be written as

$$\begin{gathered} b_{\rm X}(c,T) = (1-c)^2 \exp\left[\sum_{n=1} z_n^{sp} \ln(1 + f_n^{sp} c)\right], \\ f_n^{sp} = \exp(-\beta \Delta_n) - 1, \end{gathered} \tag{78}$$

where z_n^{sp} is the coordination number and Δ_n is the saddle-point interaction for the nth coordination sphere of the saddle point considered. If these interactions are weak, $\beta \Delta_n \ll 1$, then Eq. (78) takes its MFA form

$$b_{\rm X}(c,T) = (1-c)^2 \exp\left(-\beta c \sum_{n=1} z_n^{sp} \Delta_n\right). \tag{79}$$

But for the realistic saddle-point interactions Δ_n, such as those in Table 2 below, using the MFA can lead to significant errors, just as for λ in Eq. (77).

Microscopic relation (75) can be compared with various phenomenological models for diffusivity [1–4]. In particular, it can provide a statistical expression for the phenomenological mobility $M_{\rm CVa}$ introduced by Ågren in his discussion of diffusion of carbon in austenite [1–3]. Comparing Eq. (75) with the definition of $M_{\rm CVa}$ in Eq. (9) in [2], we find

$$M_{\rm CVa} = \frac{\gamma a^2 b_{\rm X}\, a_{\rm C}}{c(1-c) V_m T}, \tag{80}$$

where V_m is the volume per atom Me. In more detail, the microscopic and phenomenological descriptions of diffusion of carbon in austenite are compared in Sec. 4.

We now consider a multicomponent interstitial alloy (Me$_1$Me$_2$ ...)-X with several species atoms p in the metal sublattice, such as an Fe–Mn–C alloy. The interstitial sites are denoted by indices i, j, and k, while the sites in the metal sublattice, by indices l, m, and n. The total configurational Hamiltonian can be written in the form generalizing Eq. (3):

$$H^t = \frac{1}{2} \sum_{ij} v_{ij} n_i n_j + \sum_{p,il} V_{il}^p n_i n_l^p + \frac{1}{2} \sum_{pq,lm} V_{lm}^{pq} n_l^p n_m^q, \tag{81}$$

where we again omit the index X for an interstitial atom, setting $n_i^{\rm X} = n_i$, $V_{il}^{{\rm X}p} = V_{il}^p$, and $V_{ij}^{\rm XX} = v_{ij}$. As above, we discuss diffusion of only interstitial but not metal atoms, and the presence of vacancies in the metal sublattice is neglected. Therefore, occupation operators n_l^h for host metal h can be expressed in terms of those for the minority metals α similarly to Eq. (1): $n_l^h = 1 - \sum_\alpha n_l^\alpha$. The effective Hamiltonian for statistical averaging, instead of (19), takes the form

$$H_{eff} = -\sum_i \lambda_i n_i - \sum_{\alpha,l} \lambda_l^\alpha n_l^\alpha + \frac{1}{2} \sum_{ij} v_{ij} n_i n_j + \sum_{\alpha,il} v_{il}^\alpha n_i n_l^\alpha + \frac{1}{2} \sum_{\alpha\beta,lm} v_{lm}^{\alpha\beta} n_l^\alpha n_m^\beta, \tag{82}$$

where $v_{il}^\alpha = V_{il}^\alpha - V_{il}^h$, and $v_{lm}^{\alpha\beta}$ is related to V_{lm}^{pq} in (81) similarly to Eq. (5).

The equations describing diffusion of X atoms can again be derived using Eqs. (6)–(26) with appropriate generalizations and simplifications. In particular, the first equation in (18) here takes the form

$$\frac{dc_i}{dt} = \sum_{\{n_k, n_l^\alpha\}} \sum_{j(i)} \omega_{\rm X}^{eff} \Big[(1-n_i) n_j \times \times \exp\left(\beta \hat{E}_{ij}^{in} - \beta \hat{E}_{ij}^{SP}\right) - \{i \to j\}\Big] \times \times \exp\left[\beta\left(\Omega - H_{eff}\right)\right]. \tag{83}$$

Here, the saddle-point energy $\hat{E}_{ij}^{SP}$, instead of Eqs. (10) and (11), is given by the expression

$$\hat{E}_{ij}^{SP} = E_h + \sum_k \Delta_k^{ij} n_k + \sum_{\alpha l} \Delta_{\alpha l}^{ij} n_l^\alpha, \tag{84}$$

where Δ_k^{ij} and $\Delta_{\alpha l}^{ij}$ are analogues of Δ_k^{ij} in (67). Using relations (20) and (26), we again reduce Eq. (83) to

Table 1. Configurational interactions v_n (in kelvin) of carbon atoms in austenite

n	1	2	3	4	5	6	7	8	9	10	11
$2\mathbf{R}_n/a$	110	200	211	220	310	222	321	400	330	411	420
R_n/R_1	1	1.41	1.73	2	2.24	2.45	2.65	2.83	3	3	3.16
z_n	12	6	24	12	24	8	48	6	12	24	24
v_n^B, Blanter [16]	1334	1961	−487	46	46	267	−23	−139	58	−12	−23
v_n, this work	1400	1180	−322	46	46	267	−23	−139	58	−12	−23

Table 2. Saddle-point interactions $\Delta_n = \Delta(\mathbf{R}_n^{sp})$ (in kelvin) of carbon atoms in austenite for vectors $\mathbf{R}_n^{sp} = \mathbf{R}_n' - \mathbf{R}_{sp}$, where $\mathbf{R}_{sp}$ is the saddle-point position of the carbon atom

n	1	2	3	4	5	6	7	8	9	10
R_n^{sp}/R_1	0.87	1.12	1.32	1.5	1.66	1.80	1.94	2.06	2.18	2.29
z_n^{sp}	4	4	8	6	4	12	8	8	12	8
Δ_n	1470	1336	1228	229	−924	−929	−543	133	133	286

n	11	12	13	14	15	16	17	18	19
R_n^{sp}/R_1	2.40	2.50	2.60	2.70	2.78	2.87	2.96	3.04	3.12
z_n^{sp}	8	14	16	4	16	16	8	20	8
Δ_n	622	564	144	−160	−310	−269	34	−43	−59

form (65). However, the activation energy E_{ac} in (66) and the correlator b_{ij}^{X} in (67) are now defined as

$$E_{ac} = E_h - \sum_l V_{il}^h,$$
$$b_{ij}^{\mathrm{X}} = \left\langle (1-n_i)(1-n_j) \times \right. \tag{85}$$
$$\left. \times \exp\left(-\beta \sum_k \Delta_k^{ij} n_k - \beta \sum_{\alpha l} \Delta_{\alpha l}^{ij} n_l^{\alpha} \right) \right\rangle,$$

and Eqs. (83) and (85) now include statistical averaging over various distributions of α-species atoms in the metal sublattice.

4. CALCULATIONS OF DIFFUSIVITY AND ACTIVITY OF CARBON IN AUSTENITE FOR SIMPLE MODELS OF CARBON–CARBON INTERACTIONS

To calculate the diffusivity D in accordance with microscopic expression (75), we should use some theoretical model of X–X interactions in an alloy, both for the configurational interactions v_n in (77), which determine the chemical potential λ, and for the saddle-point interactions Δ_n in (79), which determine the correlator b_{X}. For substitution Fe–Cu alloys, such a first-principle model for both v_n and Δ_n was developed in [14], and simulations of precipitation in Fe–Cu alloys based on this model confirmed its relevance and reliability [14]. For interactions of carbon in austenite, reliable first-principle calculations are still absent due to the well-known difficulties of taking magnetic interactions in γ-iron into account [19]. However, some simplified model of configurational interactions v_n in austenite has been suggested by Blanter [16], and his estimates of these interactions are presented in Table 1 as v_n^B. Below, we use this model and some its extensions to investigate the concentration and temperature dependences of the diffusivity D that follow from microscopic expression (75).

Blanter used the model of purely deformational configurational interactions with the nearest-neighbor Kanzaki forces for all constants v_n^B except the first one. The nearest-neighbor constant v_1^B (which cannot be described by the deformational model correctly due to the

strong "chemical" repulsion at short C–C distances) was treated as a free parameter, which was estimated from the fit of the carbon activity in austenite with respect to graphite, $a_{\rm C}^{\gamma-gr}$, calculated with these v_n^B to the experimental values. The quantity $a_{\rm C}^{\gamma-gr}$ is related to the "configurational" activity $a_{\rm C} = \exp(\beta\lambda_{\rm C})$, where $\lambda_{\rm C} = \lambda$ is the chemical potential of carbon in austenite discussed in Sec. 3, by the thermodynamic relation [16]

$$a_{\rm C}^{\gamma-gr} = a_{\rm C}\exp(\beta\Delta G_{\rm C}^{\gamma-gr}), \tag{86}$$

where $\Delta G_{\rm C}^{\gamma-gr} = \Delta G_{\rm C}^{\gamma-gr}(T)$ is the difference between the thermodynamic potentials per carbon atom in a pure γ-iron and in graphite. The fit to the experimental $a_{\rm C}^{\gamma-gr}(c,T)$ values obtained with the use of both Monte Carlo [16] and PCA [29] calculations of $a_{\rm C}(c,T)$ the v_n^B values, and for $\Delta G_{\rm C}^{\gamma-gr}(T)$, some experimental estimates, seemed to be quite satisfactory. This may imply that the simple model of Blanter [16] can serve as a basis for realistic descriptions of C–C interactions in austenite.

We estimated the configurational interactions v_n using a similar approach. However, in the fit to experimental $a_{\rm C}^{\gamma-gr}(c,T)$ values, we estimated the function $\Delta G_{\rm C}^{\gamma-gr}$ in (86) using the interpolation of experimental data suggested by Ågren [36]:

$$\Delta G_{\rm C}^{\gamma-gr} = 5550\,{\rm K} - 2.31\,T \tag{87}$$

instead of the interpolation in [29], and we also varied not only v_1 but also the next two constants, v_2 and v_3. The v_n values obtained are presented in the last line of Table 1. Variations of our v_2 and v_3 with respect to their "purely deformational" values v_2^B and v_3^B lie certainly within the real accuracy of the original Blanter model because, first, this model disregards "chemical" contributions to v_2 and v_3, which can be quite noticeable (which is illustrated, in particular, by comparing the results of calculations of C–C interactions in ferrite based on *ab initio* [20] and on purely deformational [37] approaches [33]) and, second, it neglects both possible contributions of non-nearest Kanzaki forces [29] and a probable variation of phonon spectra with temperature (which was not measured in γ-iron but is very pronounced in BCC iron [34, 35]). In Figs. 1 and 2, we present the carbon activity $a_{\rm C}^{\gamma-gr}(x_{\rm C},T)$ and the equilibrium ferrite–austenite phase diagram calculated using PCA expression (77) for λ with our v_n from Table 1, together with experimental data and the results of calculations based on the phenomenological model by Ågren [36].

We now discuss the saddle-point interactions $\Delta_n = \Delta(\mathbf{R}_n^{sp})$, where $\mathbf{R}_n^{sp} = \mathbf{R}'_n - \mathbf{R}_{sp}$, and $\mathbf{R}_{sp}$ is the

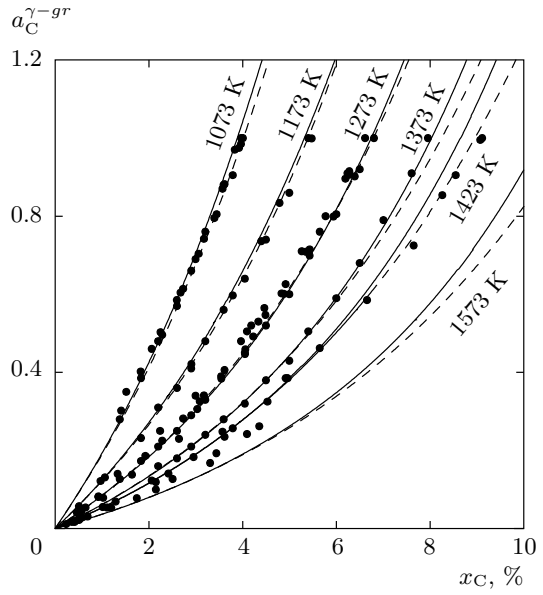

Fig. 1. Dependence of the carbon activity $a_{\rm C}^{\gamma-gr}$ in austenite with respect to graphite on the carbon concentration $x_{\rm C} = c/(1+c)$ for various temperatures T. Dots correspond to the experimental data in [16]. Solid curves are calculated using PCA expression (77) for λ with the interaction constants v_n from Table 1. Dashed curves are calculated using the phenomenological description of C–C interactions used by Ågren [36]

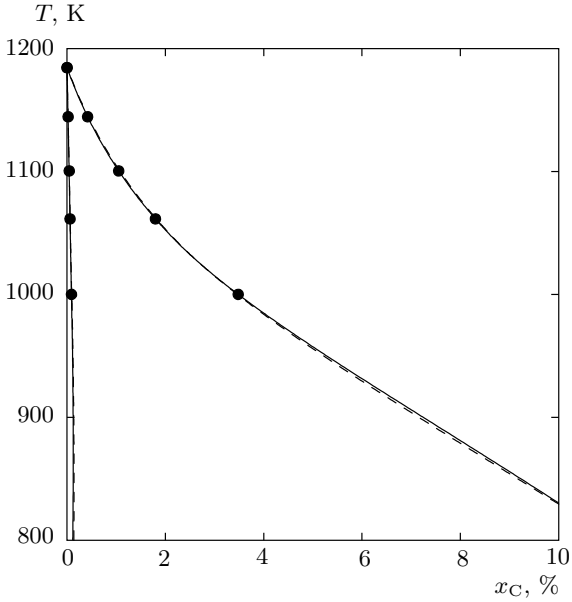

Fig. 2. Fe–C phase diagram. Dots correspond to experimental phase boundaries. Solid curves show ferrite–austenite phase boundaries calculated using Eq. (77) with v_n from Table 1. Dashed curves correspond to the phenomenological calculations by Ågren [36]

saddle-point position of the carbon atom. In the second and third lines of Table 2, we show the first 19 distances $R_n^{sp} = |\mathbf{R}_n^{sp}|$ and the coordination numbers z_n^{sp} that correspond to these $\mathbf{R}_n^{sp}$. To illustrate the distribution of the $\mathbf{R}_n^{sp}$ vectors in the FCC lattice, we present the values of components of lattice vectors $\mathbf{R}'_n = \mathbf{R}_n^{sp} + \mathbf{R}_{sp}$ (in $a/2$ units) for the first eight coordination spheres of the point $\mathbf{R}_{sp} = (0.5, 0.5, 0)$:

$$\begin{aligned}
\mathbf{R}'_1 &= (0,1,\pm1),(1,0,\pm1),\\
\mathbf{R}'_2 &= (0,2,0),(2,0,0),(1,\bar1,0),(\bar1,1,0),\\
\mathbf{R}'_3 &= (2,1,\pm1),(1,2,\pm1),(0,\bar1,\pm1),(\bar1,0,\pm1),\\
\mathbf{R}'_4 &= (2,2,0),(\bar1,\bar1,0),(0,0,\pm2),(1,1,\pm2),\\
\mathbf{R}'_5 &= (2,\bar1,\pm1),(\bar1,2,\pm1),\\
\mathbf{R}'_6 &= (0,\bar2,0),(\bar2,0,0),(1,3,0),\\
&\quad (3,1,0),(0,2,\pm2),\\
&\quad (2,0,\pm2),(1,\bar1,\pm2),(\bar1,1,\pm2),(\bar1,1,\pm3),\\
\mathbf{R}'_7 &= (0,3,\pm1),(3,0,\pm1),(\bar2,1,\pm1),\\
&\quad (1,\bar2,\pm1),(3,0,\pm1),\\
\mathbf{R}'_8 &= (2,\bar2,0),(\bar2,2,0),(3,\bar1,0),(\bar1,3,0),\\
&\quad (0,1,\pm3),(\bar1,\bar1,\pm1).
\end{aligned} \tag{88}$$

Models for estimating the saddle-point interactions Δ_n can be constructed similarly to those for the configurational interactions v_n. The long-range deformational contributions to Δ_n can be calculated using the general expression for deformational interactions with arbitrary Kanzaki forces discussed in [29], while the short-range chemical contributions can be estimated by treating the first several Δ_n as adjustable parameters, as this was done for the v_n. However, we here restrict ourselves by illustrative estimates of Δ_n based on some interpolations between the v_n values in Table 1 and on several simple assumptions. First, we assume that both chemical and deformational contributions to Δ_n depend only on the distance $R_n^{sp} = |\mathbf{R}_n^{sp}|$ and vary with R_n^{sp} smoothly. Second, we assume that for short distances $R_n^{sp} < R_2 = 1.41R_1$, the Δ_n values are mainly determined by the chemical contributions, while for $R_n^{sp} > R_2$, these values are mainly determined by the deformational contributions. Third, we assume that the dependence the saddle-point interactions Δ_n on R_n^{sp} is similar to the dependence of the configurational interactions v_n on R_n, for both chemical and deformational contributions. Then the "chemical" interactions Δ_1, Δ_2, and Δ_3 can be estimated using the linear interpolation between v_1 and v_2 values, as shown in Figs. 3 and 4. For the "deformational" Δ_n with $n \geq 4$

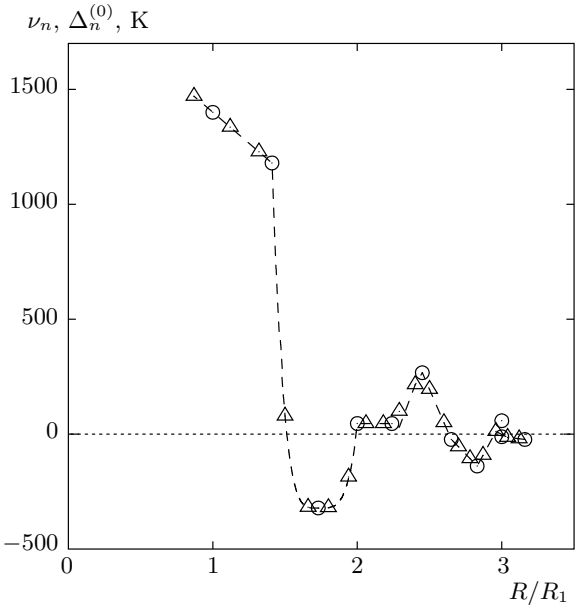

Fig. 3. Illustration of our method of estimates of saddle-point interactions Δ_n using the interpolation of configurational interactions $v_n = v(R_n)$. Circles show the values of v_n and triangles, the values of $\Delta_n^{(0)}$ obtained as described in the text

or $R_n^{sp} > R_2$, the analogous estimate of Δ_n includes the following two steps.

(A) Interpolation of the dependence $v(R)$ using the v_n values in Table 1, which yields the "preliminary" values $\Delta_n^{(0)}$ shown in Fig. 3.

(B) Scaling of these $\Delta_n^{(0)}$ by some factor α,

$$\Delta_n = \alpha \Delta_n^{(0)}, \tag{89}$$

with the value of α determined from the fit of the diffusivity D calculated according to Eqs. (75)–(79) to the experimental data about the diffusivity of carbon in austenite.

Step A is illustrated in Fig. 3. This figure shows that to obtain an appropriate interpolation $v(R)$, the regions of long and "intermediate" distances R should be treated differently. At long distances $R > R_4$, we can use the simple linear interpolation between neighboring v_n values, while at $R_2 < R < R_4$, some smooth curve should be drawn between v_2, v_3, and v_4 values. For these intermediate R, we interpolate $v(R)$ by a simple power law:

$$v(R) = \begin{cases} C_2(R_3 - R)^m, & R_2 < R < R_3, \\ C_4(R - R_3)^m, & R_3 < R < R_4, \end{cases} \tag{90}$$

where constants C_2 and C_4 are determined by the conditions $v(R_2) = v_2$ and $v(R_4) = v_4$. For the exponent

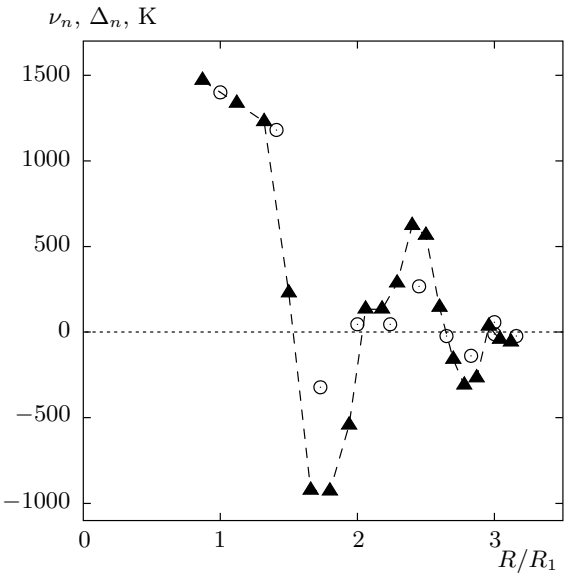

Fig. 4. Values of C–C interactions that we use. Open circles: configurational interactions $v_n = v(R_n)$; black triangles: saddle-point interactions $\Delta_n = \Delta(R_n^{sp})$. Dashed lines connect the neighboring Δ_n values to guide the eye

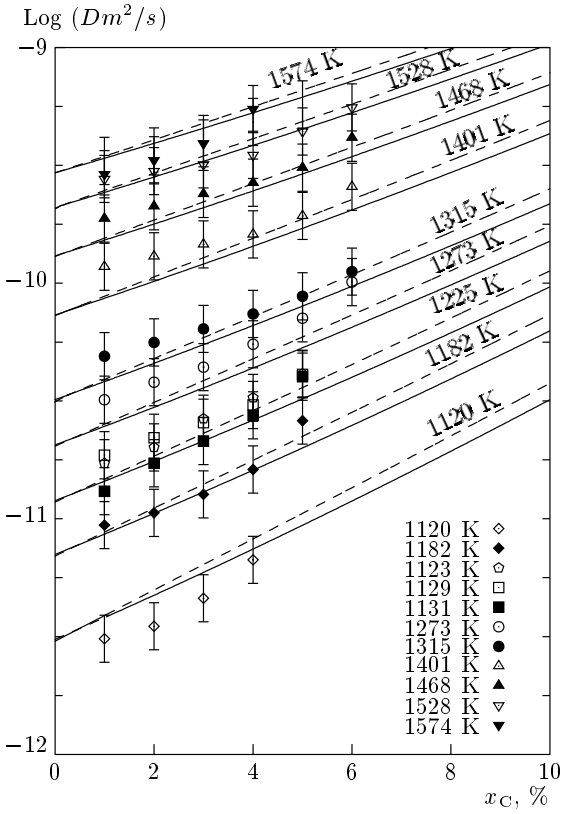

Fig. 5. The diffusivity $D_C(x_C, T)$ of carbon in austenite. The symbols show experimental values from [38] presented in [3]. The solid lines are calculated using Eq. (75) and the v_n and Δ_n values from Tables 1 and 2. The dashed lines show the results of calculations by Ågren [3] based on his phenomenological model

m we tried two values, 2 and 4, and the value $m = 4$ was found to be more suitable for the fit involved in step B. The resulting interpolation $v(R)$ is shown in Fig. 3 by the dashed curve.

For step B, the physical arguments in favor of model relation (89) can be deduced from the general expression for deformational interactions in Eq. (11) in [29]. According to this expression, the deformational interaction $V_{ij}^d = V^d(\mathbf{R}_i - \mathbf{R}_j)$ between two atoms positioned at $\mathbf{R}_i$ and $\mathbf{R}_j$ is proportional to the integral over wave-numbers $\mathbf{k}$ in the Brillouin zone of some expression that includes the product of two appropriate Kanzaki forces, $\mathbf{f}_\mathbf{k}^i$ and $\mathbf{f}_\mathbf{k}^j$, while each of these forces is proportional to the amplitude of displacements of neighboring host (iron) atoms due to the presence of an impurity (carbon) atom at the site i or j. Therefore, for the configurational interactions v_n, the deformational contributions are proportional to the product of two Kanzaki forces $\mathbf{f}_i^{op}$ and $\mathbf{f}_j^{op}$ that describe the displacements of iron atoms induced by a carbon atom located in the octo-pore. At the same time, for the saddle-point interaction Δ_n, one of these factors is replaced by a Kanzaki force $\mathbf{f}_i^{sp}$ that describes the analogous displacements of iron atoms induced by a carbon atom in the saddle-point position, for which the carbon–iron distance $R_{\mathrm{Fe-C}}$ is $1/\sqrt{2}$ times that for a carbon atom in an octo-pore. Therefore, this Kanzaki force $\mathbf{f}_i^{sp}$ can be expected to considerably exceed $\mathbf{f}_i^{op}$. Hence, the factor α in (89), which qualitatively describes the relative scale of deformational contributions to the v_n and Δ_n values, can considerably exceed unity.

The description of available experimental data on the diffusivity $D_C(x_C, T)$ [38] by our model with the choice $\alpha = 2.9$ in Eq. (89) is shown in Fig. 5. This description corresponds to the following values of the saddle-point energy E_{ac}, the product $\omega_C^{eff} a^2$, and the frequency ω_C^{eff} in Eqs. (75) and (76):

$$E_{ac} = 17700 \text{ K}, \tag{91}$$

$$\begin{aligned} \omega_C^{eff} a^2 &= 0.225 \text{ cm}^2/\text{sec}, \\ \omega_C^{eff} &= 1.76 \cdot 10^{14} \text{ sec}^{-1}, \end{aligned} \tag{92}$$

where the value $a = 3.58$ Å for γ-iron [40] is used. We note that the choice $\alpha = 3.04$ in Eq. (89) would yield the values of $D_C(x_C, T)$ that virtually coincide

with those obtained by Ågren [3]. However, the choice $\alpha = 2.9$ seems to better describe the low-temperature data in [38], which agree with those obtained in [39]. The saddle-point interactions Δ_n that correspond to $\alpha = 2.9$ are presented in Table 2 and Fig. 4.

Both experimental and theoretical results presented in Fig. 5 show that the diffusivity $D_{\rm C}$ sharply increases as the carbon concentration $x_{\rm C}$ increases. In accordance with Eqs. (10), (11), (75), and (79), this seems to indicate the presence of a significant attraction in the saddle-point interactions Δ_n, because this attraction decreases the saddle-point energy $E_{\rm C}^{SP}$ for the intersite jumps of carbon atoms. In the model estimates of interactions shown in Fig.4, it corresponds to the presence of significant negative Δ_n at "intermediate" C–C distances R in the range $1.6R_1 \lesssim R \lesssim 2R_1$. The increase in $D_{\rm C}(c,T)$ with $x_{\rm C}$ mentioned above can imply that such a significant attraction is present not only in our model estimates but also in the real saddle-point interactions of carbon atoms in austenite.

We now discuss the values of the pre-factor $\omega_{\rm C}^{eff}$ and the "transition state entropy" $\Delta S_{\rm C}^{SP}$ in (8) that correspond to estimate (92). The attempt frequency ω_{pv} in (8) can be estimated in our case as the frequency $\omega_{\rm C}^{\gamma}$ of local vibrations of carbon in austenite. These vibrations have been experimentally studied in [41] with the result

$$\omega_{\rm C}^{\gamma} \approx 75\,{\rm meV} = 1.14 \cdot 10^{14}\,{\rm sec}^{-1}. \qquad (93)$$

Note that this $\omega_{\rm C}^{\gamma}$ exceeds the Debye frequency of γ-iron, $\omega_D^{\gamma} = 0.43 \cdot 10^{14}\,{\rm sec}^{-1}$ [42], by about three times. Then using Eq. (8) with $\omega_{pv} = \omega_{\rm C}^{\gamma}$ and $\omega_{pv}^{eff} = \omega_{\rm C}^{eff}$ from (92), we obtain

$$\Delta S_{\rm C}^{SP} \approx 0.4, \quad \bar{\omega}_{\rm C}^{sp} \approx 0.9\omega_{\rm C}^{\gamma}. \qquad (94)$$

These relations show that the "softening" of saddle-point frequencies $\omega_{\rm C}^{sp}$ with respect to $\omega_{\rm C}^{\gamma}$ for carbon in austenite is rather weak (if any), unlike for Fe–Cu substitution alloys discussed in Sec. 2.1, while the saddle-point entropy $\Delta S_{\rm C}^{SP}$ is by an order of magnitude lower than the analogous $\Delta S_{{\rm Cu}v}^{SP}$ and $\Delta S_{{\rm Fe}v}^{SP}$ values for Fe–Cu alloys (as estimated in [14]). The difference can be related (at least partly) to the above-mentioned inequality $\omega_{\rm C}^{\gamma} \gg \omega_D^{\gamma}$, which implies that the dynamics of carbon atoms in austenite is much faster than the iron atom dynamics. Under such conditions, the assumption of "a local thermodynamic equilibrium" for the saddle-point transition state, as well as the entropy notion for this state, may not be fully applicable and should be used with caution.

We note that Eqs. (94) correspond to the pre-factor $\omega_{\rm C}^{eff}$ of the factor γ in (76) that determines diffusivity (75) in the dilute alloy limit. Therefore, these equations have no relevance to the illustrative estimates of C–C interactions discussed above, but they provide some definite information about the microscopic characteristics of diffusion of carbon in γ-iron.

Finally, we compare the microscopic description of thermodynamic and diffusional characteristics of carbon in austenite presented in this work with their phenomenological description developed by Ågren [2, 3, 36]. Both approaches use a similar number of adjustable parameters, and the quality of agreement between the results obtained and the experimental data shown in Figs. 1, 2 and 5 is similar. But the microscopic approach seems to provide a better physical understanding of the phenomena considered. It also opens possibilities of developing fully first-principle descriptions with no adjustable parameters, as was demonstrated in [14] for Fe–Cu alloys. In addition, microscopic expression (75) for the diffusivity seems to elucidate a number of principal points not discussed earlier. First, it shows that the diffusivity can be written in the form of the product of "thermodynamic" and "kinetic" (or "saddle-point") factors, and the thermodynamic factors include not only the usual, so-called Darken factor $\partial \ln a_{\rm X}/\partial \ln c$ [2] but also the concentration derivative of the activity itself, $\partial a_{\rm X}/\partial c$. Second, microscopic relations (75)–(79) allow estimating the "transition state entropy" ΔS^{SP} from experimental data, as was demonstrated for carbon in austenite. Third, these microscopic relations allow relating the concentration dependence of the activity $a_{\rm X}$ and the diffusivity $D_{\rm X}$ to both the configurational and saddle-point interactions between interstitial atoms X, in particular, between carbon atoms in austenite. Therefore, the analysis of experimental data on $a_{\rm C}(x_{\rm C},T)$ and $D_{\rm C}(x_{\rm C},T)$ can lead to insights into the type and the scale of these interactions.

5. CONCLUSIONS

We summarize the main results in this work. The fundamental master equation for the probability of various atomic distrubutions in an alloy has been used to derive the basic equations of diffusional kinetics in alloys. The microscopic parameters entering these equations can be calculated by *ab initio* methods, as was demonstrated by SF for iron–copper alloys [14], or using various theoretical models. For substitution alloys, the diffusional transformation kinetics is described by the "quasi-equilibrium" kinetic equation (QKE) derived in Sec. 2.1. This equation (28) generalizes the earlier

version presented in [15] by taking possible "interaction renormalization" effects into account, which can be important for the vacancy-mediated kinetics [11, 13]. In Sec. 2.2, we described the calculations of local chemical potentials λ_i and correlators b_{ij} entering QKE (28) with the use of some analytic methods that combine the simplicity of calculations with high accuracy, especially for dilute alloys. In Sec. 2.3, we reduced QKE (28) describing the vacancy-mediated kinetics to the kinetic equation for some equivalent direct-atomic-exchange model that is suitable for computer simulations.

The microscopic equations describing diffusion of interstitial atoms X in an interstitial alloy Me–X are derived in Sec. 3. These equations have simple form (65) or (68), which allows obtaining explicit analytic expressions for the diffusivity $D = D_{\rm X}$. These expressions for D given by Eqs. (71) or (75) have a simple form of products of three factors: the concentration derivative of the thermodynamic activity $a_{\rm X}$ of atoms X, the correlator $b_{\rm X}$ given by Eqs. (67) or (79), which describes the influence of interactions between atoms X on the activation barrier for the intersite jumps of atoms X, and the concentration-independent factor γ describing the diffusivity in the dilute alloy limit. This microscopic expression for D is conspicuously different from those used in phenomenological treatments [1–4], in particular, by the presence of the concentration derivative $\partial a_{\rm X}/\partial c$ rather than the so-called Darken factor $\partial \ln a_{\rm X}/\partial \ln c$ that is written usually. We also derive equations describing diffusion of interstitial atoms X in a multicomponent alloy ($\rm Me_1Me_2$ ...)–X.

In Sec. 4, we applied the results in Sec. 3 to microscopically treat the problem of diffusion of carbon in austenite discussed by a number of authors [1–4]. Our treatment is based on the microscopic model of C–C interactions in austenite suggested in [16], which supposes a strong "chemical" repulsion at short C–C distances R and a purely deformational interaction at longer R. To estimate the configurational interactions $v(R)$ that determine the carbon activity $a_{\rm C}$ and the "saddle-point" interactions $\Delta(R)$ that determine the above-mentioned correlator $b_{\rm X} = b_{\rm C}$, we used some plausible assumptions about the dependences $v(R)$ and $\Delta(R)$, which include adjustable parameters. The interaction models obtained enable us to describe both thermodynamic and diffusional properties of carbon in austenite at the same level of accuracy as that achieved in phenomenological treatments [1–4, 36]. At the same time, the microscopic approach used allowed us to make a number of qualitative conclusions about C–C interactions and the characteristics of diffusion of carbon in austenite, in particular, about the presence of a significant C–C attraction at intermediate R and about a rather low value of the "transition state entropy" $\Delta S_{\rm C}^{SP}$ given by estimate (94).

The authors are much indebted to F. Soisson for numerous valuable discussions, as well as to G. F. Syrykh for drawing our attention to the important experiments [41]. This paper was supported by the RFBR (grant No. 09-02-00563); by the Foundation for Support of Leading Scientific Schools of Russia (grant No. NS-7235.2010.2), and by the program of Russian university scientific potential development (grant No. 2.1.1/4540).

REFERENCES

1. J. Ågren, J. Phys. Chem. Sol. **43**, 385 (1982).
2. J. Ågren, Acta Metall. **30**, 841 (1982).
3. J. Ågren, Scripta Metall. **20**, 1507 (1986).
4. H. K. D. H. Bhadeshia, Met. Sci. **15**, 477 (1981).
5. P. Thibaux, A. Metenier, and C. Xhoffer, Met. Mater. Trans. A **38**, 1169 (2007).
6. L. Onsager, Phys. Rev. B **37**, 405 (1931); **38**, 2265 (1931).
7. G. Martin, Phys. Rev. B **41**, 2279 (1990).
8. V. G. Vaks, S. V. Beiden, and V. Yu. Dobretsov, Pis'ma v Zh. Eksp. Teor. Fiz. **61**, 65 (1995).
9. V. G. Vaks, Pis'ma v Zh. Eksp. Teor. Fiz. **63**, 447 (1996).
10. K. D. Belashchenko and V. G. Vaks, J. Phys.: Condens. Matter **10**, 1965 (1998).
11. M. Nastar, V. Yu. Dobretsov, and G. Martin, Phil. Mag. A **80**, 155 (2000).
12. V. G. Vaks, Phys. Rep. **391**, 157 (2004).
13. M. Nastar, Sol. St. Phen. **172–174**, 321 (2011).
14. F. Soisson and C.-C. Fu, Phys. Rev. B **76**, 214102 (2007).
15. K. Yu. Khromov, F. Soisson, A. Yu. Stroev, and V. G. Vaks, Zh. Exp. Teor. Fiz. **139**, 479 (2011).
16. M. S. Blanter, J. Alloys Comp. **291**, 167 (1999).
17. V. G. Vaks and K. Yu. Khromov, Zh. Exp. Teor. Fiz. **133**, 115 (2008).
18. V. G. Vaks and K. Yu. Khromov, Zh. Exp. Teor. Fiz. **133**, 313 (2008).

19. D. E. Jiang and E. A. Carter, Phys. Rev. B **67**, 214103 (2003).

20. C. Domain, C. S. Becquart, and J. Foct, Phys. Rev. B **69**, 144112 (2004).

21. V. G. Vaks, I. A. Zhuravlev, and K. Yu. Khromov, Zh. Exp. Teor. Fiz. **138**, 902 (2010).

22. L. D. Landau and E. M. Lifshits, *Statistical Physics*, Nauka, Moscow (1995).

23. C. Kittel, *Introduction to Solid State Physics*, Wiley, New York (1953), Ch. 6.

24. V. G. Vaks and V. V. Kamyshenko, Phys. Lett. A **177**, 269 (1993).

25. V. G. Vaks and S. V. Beiden, Zh. Eksp. Teor. Fiz. **105**, 1017 (1994).

26. Y. Le Bouar and F. Soisson, Phys. Rev. B **65**, 094103 (2002).

27. A. D. Le Clair, *Correlation Effects in Diffusion in Solids*, in *Physical Chemistry: An Advanced Treatise*, ed. by H. Eyring, Academic, New York (1970), Vol. 10, p. 261.

28. F. Soisson, private communication.

29. V. G. Vaks and K. Yu. Khromov, Zh. Exp. Teor. Fiz. **133**, 115 (2008).

30. M. K. Miller, B. D. Wirth, and G. R. Odette, Mater. Sci. Eng. **353**, 133 (2003).

31. R. Rana, W. Bleck, S. B. Singh, and O. N. Mohanti, Mater. Lett. **61**, 2919 (2007).

32. R. P. Kolli, R. M. Wojes, S. Zaucha, and D. N. Seidman, Int. J. Mat. Res. **99**, 513 (2008).

33. V. G. Vaks and K. Yu. Khromov, Zh. Exp. Teor. Fiz. **136**, 722 (2009).

34. S. K. Satyia, R. P. Comes, and G. Shirane, Phys. Rev. B **32**, 3309 (1985).

35. J. Neuhaus, W. Petry, and A. Krimmel, Physica B **234–236**, 897 (1997).

36. J. Ågren, Metall. Trans. A **10**, 1847 (1979).

37. J. Ågren, Metall. Trans. A **9**, 753 (1978).

38. C. Wells, W. Batz, and R. F. Mehl, Trans. AIME, J. Metals **188**, 553 (1950).

39. R. P. Smith, Acta Metall. **1**, 578 (1953).

40. G. V. Kurdyumov, L. M. Utevsky, and R. I. Entin, *Transformations in Iron and Steel*, Nauka, Moscow (1977), Ch. 3.

41. V. V. Sumin, M. G. Zemlyanov, L. M. Kaputkina et al., Fizika Metallov Metallovedenie **11**, 122 (1990).

42. J. Zaretsky and C. Stassis, Phys. Rev. B **35**, 4500 (1987).