[2] Tracer Diffusion by Six-Jump-Cycles in Nonstoichiometric B2 Intermetallic Compounds

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Abstract. Tracer diffusion in non-stoichiometric B2 intermetallic compounds having antistructural disorder is investigated using the six-jump-cycle (6JC) as a fundamental diffusion unit. For non-stoichiometric compositions, the antistructural atoms are assumed to be isolated and located at *one* of the six [110]-type and [100]-type sites (as only these sites are involved in the 6JC or 2JC). The jump frequencies for the 6JC involving a perfectly ordered configuration are calculated in terms of a four-frequency-model, using the mean-first-passage concept of Arita *et al.* The jump frequency of an antistructural atom at [110] or [100]-type sites is taken to be the harmonic mean of frequencies of two successive nearest-neighbour jumps of the same kind of atoms. The expressions for the tracer diffusion coefficients are derived for both atomic components at deviations from stoichiometry, assuming that the 6JC mechanism is valid. The results are compared with Monte Carlo simulations based on single vacancy jumps and found to be in fair agreement for compositions close to stoichiometry.

Introduction

Since some intermetallic compounds offer properties of technological interest such as low density, a high strength at elevated temperatures and a high corrosion resistance [1], there has been considerable and sustained interest in the study of diffusion kinetics in these compounds. Many intermetallic compounds that are attractive for technological applications take the B2 (CsCl) structure. Accordingly, much effort has been devoted to exploring diffusion kinetics in this particular structure.

The basic diffusion mechanism in pure metals is very well established and for the most part consists of vacancy-mediated nearest neighbour jumps. The detailed mechanism of diffusion in B2 intermetallic compounds is much more complex because of the ordered structure itself and because of the additional energy involved in any mechanism that would destroy order, even if only temporarily. For B2 intermetallic compounds showing only antistructural disorder the nearest neighbour vacancy mechanism still occurs, but at high levels of order the vacancy is confined to such a limited number of paths that new concatenated mechanisms can then be identified. The most energetically favourable of these is the six-jump cycle (6JC) [2], a cycle in which the vacancy migrates along a specific path of six nearest-neighbour jumps. After the six effective jumps of the vacancy, the order in the crystal is restored but there has been net transport of matter. Several reviews of the diffusion mechanisms and associated theory in B2 intermetallics have been provided recently [3,4].

Computer simulations of various models that start only with the basic vacancy mechanism clearly show the emergence of the 6JC as the level of order increases [5,6]. Historically, theoretical formalisms based on single vacancy jumps have had difficulty in describing the tracer correlation factors at high levels of order, see the review [4]. A different starting point for a tracer diffusion formalism is to commence with the 6JC itself as the basic unit of the diffusion process. The original or 'pure' 6JC, by itself, does not allow for the participation of existing antistructural atoms produced either by non-stoichiometry (extrinsic defects) or by thermal activation. A logical extension is the antistructural atom-assisted 6JC mechanism (or A6JC). This mechanism consists of a 'pure' 6JC where the presence of an antistructural atom in a next nearest neighbour site of the vacancy lowers the activation energy barrier. This antistructural atom is not involved in any exchange with the vacancy within the 6JC. Domian and Aaronson [7] were the first to suggest such an approach to tracer diffusion in B2 intermetallics but their formalism concentrated only on the jump frequency and not tracer correlation effects.

Belova and Murch [8-10] extended this concept to describe tracer and collective diffusion in non-stoichiometric B2 intermetallic compounds by considering the antistructural atom as an 'impurity' and using the 6JC as the diffusion unit in an analogue of the well known five-frequency model for impurity diffusion via single vacancy jumps. They derived expressions for tracer and collective correlation factors and tracer and chemical diffusivities and obtained excellent agreement with results obtained Monte Carlo computer simulation of the Ising alloy model.

In the present paper, we have calculated tracer correlation factors in a non-stoichiometric and partially ordered B2 intermetallic binary compound. The linear response theory described by Allnatt and Lidiard [11] has been used to express phenomenological transport coefficients for the tracer on the two sub-lattices. The required conditional probability functions are evaluated through kinetic equations where the 6JC mechanism is used as a fundamental unit for diffusion. The results of tracer correlation factors for both atomic components at deviations from stoichiometry are compared with Monte Carlo simulation obtained for the four-frequency model. The results are also compared with those obtained from a previous calculation [12], where the coupling between the two sub-lattices was considered through random nearest-neighbour vacancy jumps only.

Average jump frequency for an isolated 6JC

In the Ising alloy model, the occurrence of order is due to the imposed interactions between the atoms [13,14]. In the simplified 'four-frequency' model (where there is no explicit interaction between atoms except one atom per site), the two sub-lattices exist *a priori* [15]. Each sub-lattice is considered as a random alloy but in general the two sub-lattices take different compositions. We consider sublattice-1 as the home sub-lattice of atoms of type B and sublattice-2 as the home sub-lattice of atoms of type A. Then B_1 and A_1 respectively denote the regular and antistructural atoms on sublattice-1 whereas A_2 and B_2 respectively denote the regular and antistructural atoms on sublattice-2. With two types of vacancies (V_1 = vacancy on sublattice-1 only and V_2 = vacancy on sublattice-2 only), there will be four jump frequencies denoted by $W_{B_1} \equiv W_B^{1 \rightarrow 2}$, the atom-vacancy exchange frequency when a B atom is on sublattice-1 and a vacancy is at its nearest-neighbour site (on sublattice-2). Likewise, we define $W_{A_1} \equiv W_A^{1 \rightarrow 2}$, $W_{A_2} \equiv W_A^{2 \rightarrow 1}$, $W_{B_2} \equiv W_B^{2 \rightarrow 1}$. Similarly for the tracer atom, we have $W_{T_1} \equiv W_T^{1 \rightarrow 2}$ and $W_{T_2} \equiv W_T^{2 \rightarrow 1}$ depending upon whether the tracer is on sublattice-1 or sublattice-2 respectively. For the very dilute vacancy and tracer components, the species occupations for the four-component system can be easily obtained [15].

In the 6JC mechanism, starting from a fully ordered configuration, the vacancy progressively disorders the structure in its first three effective jumps and in its next three effective jumps the vacancy progressively re-orders the lattice resulting in the fully ordered configuration once again. By the end of the sequence of six (effective) vacancy jumps, diffusion has occurred on the same sub-lattice. For a perfectly ordered configuration, the 6JC frequency of regular atom (an

A-atom on the sublattice-2 or a B-atom on the sublattice-1) is calculated in terms of the four-frequency model, using the mean first passage concept of Arita *et al.* [16] by finding the expectation time for a vacancy to complete the cycle. The inverse of this expectation time is the average jump frequency for the 6JC. For an *isolated* 6JC, the jump frequency for the structured atom is (1/48) of this average frequency [8-10]. Following Arita *et al.* [16], we thus obtain:

$$v_{A2} \equiv v_{B1} = \frac{\alpha^3 (4\alpha^2 + 6\alpha + 3)}{(4\alpha^7 + 48\alpha^6 + 364\alpha^5 + 1360\alpha^4 + 1325\alpha^3 + 2232\alpha^2 + 1152\alpha + 288)} \quad (1)$$

Here α is the ratio of the jump frequencies of the regular and antistructural atoms of the same type. That is:

$$\alpha = \frac{W_{B1}}{W_{B2}} = \frac{W_{A2}}{W_{A1}} \quad (2)$$

For the evaluation of the jump frequency for the antistructural atom we observe that when an antistructural atom is at [110]-type or [100]-type sites relative to the vacancy, after two successive nearest-neighbour vacancy-atom exchanges, the resulting configuration has the same energy as the initial one and the net displacement of the antistructural atom is non-zero. By its very nature, the frequency of this 2JC is much greater than that of the 6JC resulting from the same energy configuration. The jump frequency for [110]-2JC or [100]-2JC involving antistructured atom can be taken to be the harmonic mean of the individual jump frequencies of two successive N-N jumps of that kind of atoms [17]. Thus, we have:

$$v_{B2} \equiv v_{A1} = \frac{2\alpha}{(1+\alpha)} \quad (3)$$

Phenomenological coefficients for the tracer

It has been recognized that when matter transport is governed by the 6JC mechanism alone, diffusion on each sub-lattice is independent of the other. Therefore, we consider only one sub-lattice, say, sublattice-1 and obtain the results for the other sub-lattice by interchanging the subscript 1 with 2. As explained earlier, the tracer diffuses at the end of the sequence of six (effective) vacancy jumps when it is at [110]-type or at [100]-type sites relative to the vacancy. We denote by v_{T1}^1 the effective tracer frequency corresponding to the single isolated [110]-cycle and by v_{T1}^0 the effective frequency corresponding to single isolated [100]-cycle (straight or bent). There are 12 equivalent [110]-type sites, denoted by the coordination number Z_1 , that give the tracer displacement $S_1 = \sqrt{2}a$ at the end of the 6JC involving these sites. Similarly there are 6 equivalent [100]-type sites, denoted by Z_0 , that give tracer displacement $S_0 = a$ at the end of [100]-straight or bent cycles. Here, a is the cube length.

We use the linear response formalism described by Allnatt and Lidiard [11] to evaluate the phenomenological transport coefficients for the tracers in B2 intermetallic compounds. The phenomenological transport coefficient L_{T1T1} (for sublattice-1) is divided into an uncorrelated part, $L_{T1T1}^{(0)}$, and a correlated part, $L_{T1T1}^{(1)}$. The uncorrelated part can be expressed as:

$$\begin{aligned} L_{T1T1}^{(0)} &= \left(\frac{N}{6kT} \right) [Z_1 S_1^2 v_{T1}^1 + 2Z_0 S_0^2 v_{T1}^0] C_{V1} C_{T1} \\ &= \left(\frac{2Na^2}{kT} \right) [2v_{T1}^1 + v_{T1}^0] C_{V1} C_{T1} \end{aligned} \quad (4)$$

The factor 2 is multiplied in the second term to account for straight and bent [100]-cycles. Here N is the number of lattice sites per unit volume, k is the Boltzmann constant and T is the absolute temperature. C_{V1} and C_{T1} respectively denote the vacancy and tracer fractional site-concentrations on the sublattice-1.

We further consider that the tracer makes a correlated random walk on a sub-lattice involving only [100]-type or [110]-type sites relative to the vacancy (since only these sites are involved in the 6JC mechanism) and also the fact that effective single 6JC frequencies for the straight and bent [100]- cycles are the same. The expression for $L_{T1T1}^{(1)}$ can be written as:

$$L_{T1T1}^{(1)} = -\left(\frac{N}{3kT}\right) \left[v_{T1}^1 v_{T1}^1 \sum_{S_1, S_1^0} S_1 \cdot S_1^0 \phi(S_1 : S_1^0) + 2v_{T1}^1 v_{T1}^0 \sum_{S_1, S_0^0} S_1 \cdot S_0^0 \phi(S_1 : S_0^0) \right. \\ \left. + 2v_{T1}^0 v_{T1}^1 \sum_{S_0, S_1^0} S_0^0 \cdot S_1^0 \phi(S_0^0 : S_1^0) + 4v_{T1}^0 v_{T1}^0 \sum_{S_0, S_0^0} S_0^0 \cdot S_0^0 \phi(S_0^0 : S_0^0) \right] \quad (5)$$

where we have defined, for example,

$$\phi(S_1 : S_0^0) = \int_0^\infty dt \sum_\lambda \psi_{V1T1:V1T1}(\lambda, \lambda - S_1; t : \lambda^0, \lambda^0 - S_0^0; t = 0) \quad (6)$$

Here $\psi_{V1T1:V1T1}(\lambda, \lambda - S_1; t : \lambda^0, \lambda^0 - S_0^0; t = 0)$ is the conditional probability of finding at time t the vacancy at site λ and the tracer at its [110]-type site ($\lambda - S_1$) when initially the vacancy was at any site λ^0 and tracer at [100]-type site ($\lambda^0 - S_0^0$) on the same sub-lattice. In order to proceed further, we follow Chaturvedi and Allnatt [18,19] and define the Fourier transform as:

$$\tilde{\phi}(\mathbf{k} : S^0) = \sum_{\mathbf{r}} e^{i\mathbf{k} \cdot \mathbf{r}} \phi(\mathbf{r} : S^0) \quad (7)$$

and the inverse Fourier transform as:

$$\phi(\mathbf{r} : S^0) = \left(\frac{a}{2\pi}\right)^3 \int d^3k e^{-i\mathbf{k} \cdot \mathbf{r}} \tilde{\phi}(\mathbf{k} : S^0) \quad (8)$$

where the integrations are over the Brillouin zones in cubic lattice. Using these definitions, Eqn. 5 can be expressed as

$$L_{T1T1}^{(1)} = -\left(\frac{2Na^2}{kT}\right) [2v_{T1}^1 v_{T1}^1 U_1(: S_1^0) + 4v_{T1}^1 v_{T1}^0 U_0(: S_1^0) + v_{T1}^0 v_{T1}^1 U_1(: S_0^0) + 2v_{T1}^0 v_{T1}^0 U_0(: S_0^0)] \quad (9)$$

In the above we have defined, for example:

$$U_0(: S_1^0) = 8i \left(\frac{a}{2\pi}\right)^3 \int d^3k \sin k_x a \tilde{\phi}(\mathbf{k} : S_1^0) \quad (10a)$$

and

$$U_1(: S_1^0) = 8i \left(\frac{a}{2\pi}\right)^3 \int d^3k \sin k_x a \cos k_y a \tilde{\phi}(\mathbf{k} : S_1^0) \quad (10b)$$

Here we have used symmetry and taken a particular value of the initial vectors S_1^0 and S_0^0 , say $S_1^0 = a(\hat{x} + \hat{y})$ and $S_0^0 = a\hat{x}$.

Kinetic Equation

In the microscopic study of diffusion in solids the kinetic equation approach has proved very useful (see, Allnatt and Lidiard [11]; Chaturvedi and Allnatt [18,19]; Sharma *et al.* [20,21]). The rate equation for the probability function $\psi_{\text{VITI}}(\lambda, \lambda - r; t)$, which is the conditional probability of finding at time t the vacancy at site λ and the tracer at site $(\lambda - r)$ when the system was in the given initial state, can be written as:

$$\begin{aligned} \frac{d\psi_{\text{VITI}}(\lambda, \lambda - r)}{dt} = & \{v_{\text{TI}}^1 \theta_1(r) + 2v_{\text{TI}}^0 \theta_0(r)\} [\psi_{\text{VITI}}(\lambda - r, \lambda) - \psi_{\text{VITI}}(\lambda, \lambda - r)] \\ & + \sum_n \sum_{r' \neq r} \{v_{\text{nI}}^1 \theta_1(r') + 2v_{\text{nI}}^0 \theta_0(r')\} [\psi_{\text{VITI}_{\text{nI}}}(\lambda - r', \lambda - r, \lambda) - \psi_{\text{VITI}_{\text{nI}}}(\lambda, \lambda - r, \lambda - r')] \end{aligned} \quad (11)$$

Here n denotes the atomic species A and B. $\theta_1(r)$ is the step function which is unity when $r = S_1$ and zero otherwise. Similarly, $\theta_0(r)$ is the step function which is unity when $r = S_0$ and zero otherwise. To solve Eqn. 11 we use the simplest approximation, i.e., we express the atomic occupancy variables in terms of their average value and neglect the fluctuations from it. Furthermore we add and subtract terms with $r' = r$ in the second term of Eqn. 11. After integrating with respect to time t and summing over λ we finally obtain:

$$\begin{aligned} - \sum_{\lambda} \psi_{\text{VITI}}(\lambda, \lambda - r; t = 0) = & \{v_{\text{TI}}^1 \theta_1(r) + 2v_{\text{TI}}^0 \theta_0(r)\} \{\varphi(-r) - \varphi(r)\} \\ & + \sum_n c_{\text{nI}} \{v_{\text{nI}}^1 \theta_1(r) + 2v_{\text{nI}}^0 \theta_0(r)\} \varphi(r) \\ & + \sum_n c_{\text{nI}} \sum_{r'} \{v_{\text{nI}}^1 \theta_1(r') + 2v_{\text{nI}}^0 \theta_0(r')\} \{\varphi(r - r') - \varphi(r)\} \end{aligned} \quad (12)$$

Now, multiplying both sides by e^{ikr} and summing over r , we soon get:

$$\begin{aligned} \tilde{\varphi}(k) = & \frac{1}{v_{\text{VI}} D(k)} \left[\sum_r e^{ikr} \sum_{\lambda} \psi_{\text{VITI}}(\lambda, \lambda - r; t = 0) \right. \\ & + \left(\frac{a}{2\pi} \right)^3 \int d^3k' \{v_{\text{TI}}^1 \theta_1(k + k') + 2v_{\text{TI}}^0 \theta_0(k + k')\} \tilde{\varphi}(k') \\ & \left. + \left(\frac{a}{2\pi} \right)^3 \int d^3k' \{ (v_{\text{VI}}^1 - v_{\text{TI}}^1) \theta_1(k - k') + 2(v_{\text{VI}}^0 - v_{\text{TI}}^0) \theta_0(k - k') \} \tilde{\varphi}(k') \right] \end{aligned} \quad (13)$$

where we have defined

$$D(k) = \left[\{Z_1 - \theta_1(k)\} + \frac{v_{\text{VI}}^0}{v_{\text{VI}}^1} \{Z_0 - 2\theta_0(k)\} \right] \quad (14)$$

and

$$v_{\text{VI}}^{1(0)} = C_{\text{A1}} v_{\text{A1}}^{1(0)} + C_{\text{B1}} v_{\text{B1}}^{1(0)} \quad (15)$$

Here v_{V1}^1 and v_{V1}^0 are the average vacancy jump frequencies corresponding to the [110]-type and [100]-type sites respectively. Now, using Eqn. 13 in Eqn. 10a and following the procedure of Sandhu *et al.* [12], we get a linear equation in the U's as:

$$a_{11}U_0 + a_{12}U_1 = V^{(0)} \quad (16)$$

where

$$V^{(0)} = 8i \left(\frac{a}{2\pi} \right)^3 \int d^3k \frac{\sin k_x a}{D(k)} \sum_r e^{ik \cdot r} \sum_{\lambda} \psi_{V1T1}(\lambda, \lambda - r; t = 0) \quad (17)$$

$$a_{11} = \left\{ v_{V1}^1 - \frac{1}{2} J_2 (v_{V1}^0 - 2v_{T1}^0) \right\} \quad (18a)$$

$$a_{12} = -J_1 \{ v_{V1}^1 - 2v_{T1}^1 \} \quad (18b)$$

Since in the Manning [22,23] random alloy model, the evaluation of the static correlation functions is trivial, $V^{(0)}$ can be evaluated easily for a given initial state. For example:

$$V^{(0)}(:S_1^0) = -J_1 C_{V1} C_{T1} \quad (19a)$$

$$V^{(0)}(:S_0^0) = -J_2 C_{V1} C_{T1} \quad (19b)$$

In the above, J_1 and J_2 are the integrals that can be obtained from

$$J = 8 \left(\frac{a}{2\pi} \right)^3 \int d^3k \frac{\sin^2 k_x a}{D(k)} e(k) \quad (20)$$

when the function $e(k)$ is replaced by $\cos(k_y a)$ and 1 respectively. In order to obtain U_0 and U_1 for a given initial configuration we need another equation in addition to Eqn. 16. Substitution of Eqn. 13 in Eqn. 10b, and following the above procedure, we get:

$$a_{21}U_0 + a_{22}U_1 = V_1^{(0)} \quad (21)$$

where

$$a_{21} = -\frac{1}{2} J'_2 \{ v_{V1}^0 - 2v_{T1}^0 \} \quad (22a)$$

$$a_{22} = \{ v_{V1}^1 - J'_1 (v_{V1}^1 - 2v_{T1}^1) \} \quad (22b)$$

The function $V_1^{(0)}$ can be obtained from $V^{(0)}$ (Eqn. 17) if we replace $\sin k_x a$ in the integrand by $\sin k_x a \cos k_y a$. Similarly, J'_1 and J'_2 can be obtained from the general integral J if we replace $e(k)$ by $\cos^2 k_y a$ and $\cos k_y a$ respectively. Thus all the U's required in Eqn. 9 for the evaluation of the correlated part of the phenomenological coefficient can be obtained:

$$U_1(:S_1^0) = -\frac{(a_{22}J_1 - a_{12}J'_1)}{(a_{11}a_{22} - a_{12}a_{21})} C_{V1} C_{T1} \quad ; \quad U_1(:S_0^0) = \frac{(a_{22}J_2 - a_{12}J'_2)}{(a_{22}J_1 - a_{12}J'_1)} U_1(:S_1^0) \quad (23a)$$

$$U_0(:S_1^0) = -\frac{(a_{21}J_1 - a_{11}J'_1)}{(a_{22}J_1 - a_{12}J'_1)} U_1(:S_1^0) \quad ; \quad U_0(:S_0^0) = -\frac{(b_1J_2 - a_{11}J'_2)}{(a_{11}a_{22} - a_{12}a_{21})} U_1(:S_1^0) \quad (23b)$$

The tracer correlation factor is given by:

$$f_{T1} = 1 + \frac{L_{T1T1}^{(1)}}{L_{T1T1}^{(0)}} \quad (24)$$

Since the dynamics of the two sub-lattices is completely independent in the present model, the tracer correlation factor f_{T2} can be obtained from Eqn. 24 by inspection. The tracer correlation factor f_T for the B2 intermetallic compound is then given by the harmonic mean of the two correlation factors as [17]:

$$\frac{1}{f_T} = \frac{1}{2} \left(\frac{1}{f_{T1}} + \frac{1}{f_{T2}} \right) \quad (25)$$

Results and Discussion

The Monte Carlo simulations for the four-frequency model have been carried out using standard procedures, see for example [15]. For a general review of Monte Carlo computer simulation of diffusion kinetics, see [24]. The equilibrium composition of A atoms was varied from 0.3 to 0.5. The results for the tracer correlation factors f_A and f_B were obtained by varying the ratio of jump frequencies of regular and antistructural atoms, *i.e.*, taking $W_{A1}=W_{B2}=1$ and $W_{A2}=W_{B1}=\alpha$ for different values of α .

In order to compare the results of our expressions with those of the Monte Carlo simulation, we first consider the sublattice-1 which is the home sub-lattice for B atoms. As an approximation, we replace tracer frequencies by those of A and B atoms discussed in above. With this approximation, the frequencies v_{T1}^1 and v_{T1}^0 are equal and the J integrals become independent of frequencies. For example, when $T=A$, then v_{T1}^1 and v_{T1}^0 will be equal to the frequency of antistructural atom given by 2JC; whereas for $T=B$, these will be equal to the frequency of the regular atom given by the 6JC mechanism, obtained through the procedure of Arita *et al.* [16]. The values of J_1 and J_2 turn out to be 0.0259 and 0.2416, whereas those of J'_1 and J'_2 are 0.1252 and 0.0259 respectively.

The results of the tracer correlation factors for A atoms are presented as a function of C_A (near stoichiometry) for various values of α in Fig. 1a-d and for B atoms in Fig 2a-d. Our results (solid curves) are compared with Monte Carlo simulations (asterisks) and with those obtained by Sandhu *et al.* [12] (dashed curve). Our results are in reasonable agreement with the simulation results even when the ratio of the frequencies of the regular to antistructural atoms decreases to 0.1. The agreement is better for f_A compared with f_B . For a different comparison of the 6JC mechanism with the nearest neighbour vacancy jump approach, we have shown in Fig. 3 the dependence of f_A on α for fixed values of C_A covering the very wide range 0.3 to 0.5. It is clear that the Monte Carlo values of correlation factors for the minority component (A) are largely independent of composition. However, this feature is not followed by the present results. The dependence of f_B on α for fixed values of C_A is shown in Fig. 4. In this case the Monte Carlo values for the majority component (B) show a strong dependence on composition. The present results show an even stronger dependence. Overall, it is interesting to note that the 6JC mechanism gives qualitatively similar results to that for the independent vacancy mechanism. It is noted that in Fig. 3 the terminal point for f_A when $\alpha \rightarrow 0$ behaves in the same sort of manner as for the Monte Carlo simulation. The terminal point for f_B is analogous to f_A at the stoichiometric composition only. As C_A decreases the terminal point for f_B when $\alpha \rightarrow 0$ is no longer zero [15]. This is due to the fact that B is the majority component and B atoms will occupy a large portion of the two sub-lattices forming a network of B atoms [25]. The correlation factors of Sandhu *et al.* [12] become negative as the frequency ratio α in the range from 0.4 to 0.3 showing that the random alloy model is overestimating the tracer correlation effects when the formation of antistructural atoms is restricted.

Fig. 1. Correlation factor f_A as a function C_A for (a) $\alpha = 0.9$, (b) $\alpha = 0.7$, (c) $\alpha = 0.5$ and (d) $\alpha = 0.1$ Monte Carlo simulation -*, solid lines – results (present method), dashed lines – results of calculations by Sandhu *et al.* [12].

Fig. 2. Correlation factor f_B as a function C_A for (a) $\alpha = 0.9$, (b) $\alpha = 0.7$, (c) $\alpha = 0.5$ and (d) $\alpha = 0.1$ Monte Carlo simulation -*, solid lines – results of calculations by present method, dashed lines – results of calculations by method of Sandhu *et al.* [12].

Figure 3. Correlation factor f_A as a function of α for the B2 intermetallic compound. Solid line: present calculations for $C_A = 0.3, 0.4, 0.5$. Symbols: Monte Carlo simulation, * - for $C_A = 0.5$; x - $C_A = 0.4$; + - $C_A = 0.3$; o - results calculated by method described in Sandhu *et al.* [12] for $C_A = 0.5$.

Figure 4. Tracer correlation factor f_B as a function of α for the B2 intermetallic compound. Solid line: present calculations for $C_A = 0.3, 0.4, 0.5$. Symbols: Monte Carlo simulation, * - for $C_A = 0.5$; x - $C_A = 0.4$; + - $C_A = 0.3$; o - results calculated by method described in Sandhu *et al.* [12] for $C_A = 0.5$.

Conclusions

Tracer diffusion in non-stoichiometric B2 intermetallic compounds having antistructural disorder was investigated using the 6JC as a fundamental diffusion unit. For non-stoichiometric compositions, the antistructural atoms are assumed to be isolated and located at *one* of the six [110]-type and [100]-type sites (as only these sites are involved in the 6JC or 2JC). The jump frequencies for the 6JC involving a perfectly ordered configuration were calculated in terms of a four-frequency-model, using the mean-first-passage concept of Arita *et al.* [16]. The jump frequency of an antistructural atom at [110] or [100]-type sites was taken to be the harmonic mean of frequencies of two successive nearest-neighbour jumps of the same kind of atoms. The expressions for the tracer diffusion coefficients were derived for both atomic components at deviations from stoichiometry, assuming that the 6JC mechanism is valid. The results were compared with Monte Carlo simulations based on single vacancy jumps and found to be in fair agreement for compositions close to stoichiometry.

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Defects and Diffusion in Metals - An Annual Retrospective VIII -

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