

Diffusion in substitutionally disordered B2 intermetallics

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2002 J. Phys.: Condens. Matter 14 9563

(<http://iopscience.iop.org/0953-8984/14/41/312>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.96

The article was downloaded on 18/05/2010 at 15:10

Please note that [terms and conditions apply](#).

Diffusion in substitutionally disordered B2 intermetallics

I V Belova and G E Murch

Diffusion in Solids Group, School of Engineering, The University of Newcastle, Callaghan, NSW 2308, Australia

Received 13 August 2002

Published 4 October 2002

Online at stacks.iop.org/JPhysCM/14/9563

Abstract

In this paper, a comprehensive diffusion kinetics theory is formulated to describe seamlessly tracer and chemical diffusion in antistructurally disordered B2 intermetallics showing positive and negative deviations from stoichiometry. The theory is based around unit processes consisting of six-jump cycles that can be assisted by intrinsic and extrinsic antistructural atoms of either atomic species. The Ising alloy model is used to illustrate the formalism, but the formalism can be adapted to other models. Expressions are developed for the tracer diffusion coefficients, the phenomenological coefficients, the intrinsic diffusion coefficients, the interdiffusion coefficient and the various correlation factor components. Results for the tracer and collective correlation factors and the vacancy wind factor (in interdiffusion) are in excellent agreement with results from Monte Carlo computer simulations based around single vacancy jumps.

1. Introduction

Soon after the general acceptance that vacancies are the principal vehicles for diffusion in metals and alloys it became apparent that in the case of highly ordered intermetallics a vacancy making random nearest neighbour jumps would soon leave a trail of extensive antistructural disorder of higher energy in its wake (Elcock and McCombie 1958). To avoid this difficulty, in these compounds, a vacancy must inevitably be confined to an ever-smaller set of lower energy penalty jump sequences as the overall level of order increases. Finally, in the limit of perfect order in the special case of the stoichiometric AB alloy taking the B2 or CsCl structure, effective diffusion occurs by the vacancy moving on a six-jump-cycle (6JC) sequence. In this mechanism, starting from a fully ordered configuration the vacancy progressively disorders the structure in its first three (effective) jumps. But in its following three (effective) jumps the vacancy progressively reorders the lattice resulting in the fully ordered configuration once more (Huntington H B, private communication reported by Elcock and McCombie 1958). In the process, however, both tracer atom and matter transport occur. Furthermore, punctuating the

6JC are numerous jump reversals as many of the formed antistructural atoms return immediately to their original sites. In B2 substitutionally disordered alloys, depending on the relative contributions of the two types of 6JC in this structure, this can lead, in principle, to very small values of the tracer correlation factors for at least one atomic component. This can result in a large contribution to the overall activation energy for tracer diffusion coming from the correlation factor itself (Belova and Murch 1998, 2000a).

Computer simulations of diffusion in stoichiometric intermetallics showing substitutional disorder have clearly shown the emergence of the 6JC mechanism as the level of order increases (Arnhold 1981, Belova *et al* 1995, Athènes *et al* 1997, Belova and Murch 2000b). Importantly, fragments of the 6JC persist to relatively low levels of order with the result that the activation energy for tracer diffusion over a wide temperature range remains close to that for the 6JC itself (Belova and Murch 2000a). Some intermetallics taking the B2 structure have a tendency to exhibit structural vacancies (Chang and Neumann 1982). The presence of a high concentration of vacancies, even at stoichiometry, then makes the 6JC rather less identifiable. The present paper does not directly address such intermetallics.

A number of general formalisms based around single vacancy jumps have been developed for describing diffusion kinetics in substitutionally disordered intermetallics, see the recent review by Murch and Belova (1998) and the older review by Bakker (1984). Common to the formalisms is the major difficulty of dealing with concatenated sequences of effective vacancy jumps, in particular, the 6JC. The difficulty is manifested as rather unsatisfactory agreement with computer simulations of the tracer and collective correlation factors at low temperatures/highly ordered configurations, see for example Bakker *et al* (1976) and Belova and Murch (1996a).

Many years ago, Domian and Aronson (1964, 1965) sketched a diffusion kinetics formalism built on the 6JC itself as the basic 'unit' of the diffusion process. The neglect of correlation effects in that formalism meant that only a qualitative picture was possible. Recently, Belova and Murch (2002a, 2002b) initiated a more detailed and comprehensive approach to the problem. The original or 'pure' 6JC mechanism, *by itself*, does not allow for the participation of *existing* antistructural atoms produced either by nonstoichiometry (extrinsic defects) or by thermal activation (intrinsic defects). Belova and Murch (2002a, 2002b) proposed a natural extension of the 6JC in the intermetallic AB to allow for the participation of antistructural atoms produced by nonstoichiometry: when excess of one component, say B, is accommodated by antistructural B atoms, such atoms can contribute directly and indirectly to enhanced mobility of 6JCs. Our previous treatment dealt, in effect, with only one type of antistructural defect at a time. For, say, excess B, there is then a one-to-one correspondence between deviation from stoichiometry, δ , and fraction c_B^α of antistructural B atoms on the home lattice (α) of A atoms ($2\delta = c_B^\alpha$). Put another way, it was implied in this formalism that at the stoichiometric composition, the only possibility for atomic migration is pure 6JCs, since it is assumed there are no thermally activated antistructural atoms at this composition. Such a diffusion kinetics theory can then only be used at compositions relatively far from the stoichiometric composition.

For intermetallics that have relatively low ordering energies and exhibit only substitutional disorder, e.g. CuZn, CoFe and AgMg, there are thermally activated antistructural atoms of *both* atomic species always in coexistence at all compositions (Chang and Neumann 1982). Thus the overall deviation from stoichiometry δ should correctly be written as $2\delta = c_B^\alpha + c_B^\beta - 1$. As an aside, we might mention that an analogous feature, but involving vacancies and interstitials, occurs in some nonstoichiometric oxides such as UO_{2+x} (see, for example, Murch and Thorn (1978)). In the oxide, it means that at all compositions oxygen diffusion can be carried, in principle, by vacancies *and* interstitials, with their relative weightings dependent

on composition. In the intermetallic it means that at all compositions diffusion of either component can be carried, in principle, by pure 6JCs *and* antistructural atom assisted 6JCs, with their relative weightings dependent on composition.

Accordingly, in this paper we have extended our model (Belova and Murch 2002a, 2002b) to the general situation that encompasses antistructural disorder arising from nonstoichiometry and thermal activation (extrinsic and intrinsic antistructural disorder). Furthermore, it should also be recognized that the usual thermally activated vacancy population must also be permitted to vary with composition. To incorporate these features we extend our previous 6JC diffusion kinetics analysis by coupling it to a model for statistical disorder within the ordered state (Allnatt and Lidiard 1993). This provides a complete and seamless description of tracer and chemical diffusion via 6JCs at all compositions on both sides of stoichiometry. This is the first analytical formalism to provide this. We test the formalism with Monte Carlo computer simulation. In a subsequent paper we apply the formalism to analyse in detail the experimental tracer and chemical diffusion data in several intermetallics.

2. Theory

For convenience, in the following we make use of the Ising alloy model where there are three pair interaction energies E_{AA} , E_{BB} and E_{AB} between AA, BB and AB pairs. We define $\Delta_A = E_{AA} - E_{AB}$, $\Delta_B = E_{BB} - E_{AB}$ and $\Delta = \Delta_A - \Delta_B$; the ordering energy E is given by $E = E_{AA} + E_{BB} - 2E_{AB}$ and the asymmetry parameter U is given by Δ/E . However, we emphasize that the formalism can be adapted to other models: the main requirement is a detailed set of migration and formation energies for the variants of the 6JC involving an existing antistructural atom. For example, an embedded atom method simulation (see, for example, Mishin and Farkas 1997) could in principle provide this information. Throughout this paper the notation c_A^β is used to represent the fraction of A atoms on the β sublattice and so on.

2.1. Antistructural disorder

First, we wish to analyse antistructural disorder. Assuming a random distribution of antistructural atoms on each sublattice (the Bragg–Williams approximation) Allnatt and Lidiard (1993) provided an expression for the long-range order parameter (their equation (3.10.9)) in terms of the ordering energy E . We rewrite that expression in terms of the sublattice occupations (for convenience, we use the parameter $\delta' = (c_B^\alpha + c_A^\beta)/2$):

$$\frac{c_A^\beta c_B^\alpha}{c_A^\alpha c_B^\beta} = \exp(-8(1 - 2\delta')E/kT) \quad (1)$$

where k and T have their usual meanings. The sublattice occupations themselves are related to each other and the overall composition of B atoms c_B by

$$c_A^\alpha = 1 - c_B^\alpha; \quad c_B^\beta = 2c_B - c_B^\alpha; \quad c_A^\beta = 1 - 2c_B + c_B^\alpha \quad (2)$$

and can be obtained by substituting into and then solving equation (1) numerically.

2.2. Sublattice and overall vacancy concentrations

In order to calculate the partitioning of the vacancies between the sublattices as well as the overall vacancy site fraction we use the (Bragg–Williams approximation) relations given by Allnatt and Lidiard (1993) (see their equations (3.10.12) and (3.3.39a)). The relations were

introduced there in terms of the long-range order parameter. Again we rewrite the relations in terms of sublattice occupations as follows:

$$\frac{c_v^\alpha}{c_v^\beta} = \left(\frac{c_A^\alpha c_B^\alpha}{c_A^\beta c_B^\beta} \right)^{1/2} \exp(-4\Delta(1 - 2\delta')/kT) \quad (3)$$

and

$$c_v^\alpha c_v^\beta = \exp(-2g'_v + 8E_{AB} - 8\Delta\delta' + 8E\delta' + 8c_A^\beta c_B^\alpha E)/kT, \quad (4)$$

where $c_v^\alpha + c_v^\beta = 2c_v$, g'_v is the configuration-independent contribution to the vacancy formation energy. After solving this system of equations with respect to c_v^α and c_v^β and combining them in order to obtain c_v the overall vacancy fraction we find

$$c_v = 0.5 \left(\frac{c_A^\alpha c_B^\alpha}{c_A^\beta c_B^\beta} \right)^{1/4} \exp(-g' + 4(-\Delta c_B + 2\Delta_A \delta' - c_A^\beta c_B^\alpha E)/kT) \\ + 0.5 \left(\frac{c_A^\alpha c_B^\alpha}{c_A^\beta c_B^\beta} \right)^{-1/4} \exp(-g' + 4(\Delta c_A + 2\Delta_B \delta' - c_A^\beta c_B^\alpha E)/kT), \quad (5)$$

where $g' = g'_v - 4E_{AB}$ is constant.

2.3. Tracer diffusion coefficients

Now let us consider tracer diffusion kinetics via the 6JC. Belova and Murch (2002a, 2002b) employed the nomenclature of the well known ‘five-frequency model’ to describe the various types of jump-unit of the 6JC. This is briefly summarized in the following, but for further details Belova and Murch (2002a, 2002b) should be consulted. Consider, for example, the α -6JC (the prefix indicates the vacancy starts from the α sublattice). First, there is the ‘ w_0 jump’ which is simply the pure α -6JC itself (this leads to displacements of tracer A and B atoms). Next, the ‘ w_1 jump’, the rotational jump, is a set of four sub-types of the α -6JC that occur in roughly a rotational sense around an antistructural B atom. These α -6JCs only involve the B atom indirectly via its energy of interaction (see also Athènes *et al* 1997) and they also lead to displacements of tracer A and B atoms. Next, the ‘ w_2 jump’ is a special truncated cycle consisting of just two individual B jumps (one of which is the antistructural atom). This process has a much higher frequency than other α -6JCs. This ‘jump’ only leads to displacements of tracer B atoms. Finally, in the Ising alloy model used here both the ‘dissociation, i.e. w_3 jumps’ and ‘association, i.e. w_4 jumps’, are found to be identical to the ‘ w_0 jump’. The diffusion processes of the 6JC in the vicinity of an antistructural atom are illustrated symbolically in figure 1.

Physically, the situation for diffusion in the Ising alloy model via 6JCs can be described in the following way. There is no binding of the α -6JC vacancy to the antistructural B atom (because $w_3 = w_4$). The vacancy moves relatively slowly through the lattice, largely by isolated pure α -6JCs (w_0). When the vacancy is close to an antistructural B atom, the vacancy is engaged in either the faster rotational α -6JCs (w_1) around the antistructural B atom or even faster (w_2) jumps directly involving the B atom. It turns out that this behaviour can be expressed as

$$w_2 \gg w_1^3 > (w_1^2 + w_1^1)/2 > w_0 = w_3 = w_4, \quad (6)$$

where the superscripts on the w_1 jumps refer to the rotational jump *sub-types* mentioned above and described in detail by Belova and Murch (2002a).

For excess B compositions Belova and Murch (2002a, 2002b) divided the α -6JC into two contributions, α -6JC, 1 and α -6JC, 2 corresponding to regions 1 and 2 respectively, and

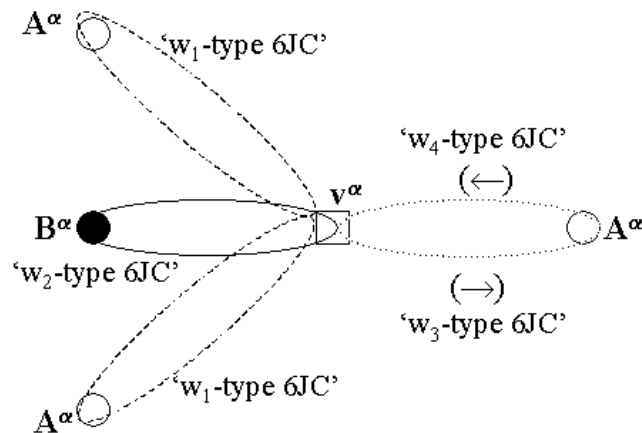


Figure 1. Symbolic representation of the basic jump types for an α -6JC in the vicinity of an antistructural B atom. The nomenclature of the five-frequency model for impurity diffusion in the fcc lattice (see, for example, Allnatt and Lidiard 1993) is used (Belova and Murch 2002a, 2002b).

analogously for the β -6JC. Region 1 refers to the region in the vicinity of an antistructural B atom and region 2 refers to the remainder of the lattice. (In effect, in region 2, diffusion is via pure 6JCs.) We now wish to generalize this by recognizing the co-existence of antistructural A and B atoms at all compositions. Then we write that region 1 refers to the region in the vicinity of an antistructural B atom and an antistructural A atom. Region 2 refers to the remainder of the lattice where both the pure α - and β -6JCs operate.

There is an assumption here that the antistructural atoms do not interact with one another. In effect, we are actually using the usual ‘very dilute approximation’, as has been employed in several other areas of diffusion research such as solute enhancement of solvent diffusion in dilute alloys (see for example Allnatt and Lidiard (1993)). There is a further assumption that there are no cross-correlations in displacements (a) between α - and β -6JCs and (b) between the two regions of a given type of 6JC. In the low temperature limit where the 6JC is operating we therefore write that the tracer diffusion coefficients can be subdivided as

$$D_{A^*} = D_{A^*}^{\alpha-6JC,1} + D_{A^*}^{\alpha-6JC,2} + D_{A^*}^{\beta-6JC,1} + D_{A^*}^{\beta-6JC,2} \quad (7)$$

and similarly for D_{B^*} .

After straightforward modification of the expressions provided by Belova and Murch (2002a, 2002b) the complete expression for the tracer diffusion coefficient of B atoms is found to be

$$D_{B^*} = \frac{a^2 \exp\{7E_{AB}/kT\}}{2c_B} (8(1 - 23\delta')(w_{0\beta}c_v^\beta + 2w_{0\alpha}c_v^\alpha) + 2c_B^\alpha c_v^\alpha [14w_{1\alpha}^3 + 25(w_{1\alpha}^1 + w_{1\alpha}^2)] + 24.1c_A^\beta c_v^\beta [w_{1\beta}^3 + 1.5(w_{1\beta}^1 + w_{1\beta}^2)]/2), \quad (8)$$

where a is the jump distance, $w_{0\beta}$ is the frequency of a pure β -6JC and so on.

$$\begin{aligned}
w_{0\beta} &= \nu \exp\{(-6E(1-2\delta') + 7c_A^\beta \Delta_A + c_B^\alpha \Delta_B)/kT\}, \\
w_{0\alpha} &= \nu \exp\{(-6E(1-2\delta') + 7c_B^\alpha \Delta_B + c_A^\beta \Delta_A)/kT\}, \\
w_{1\beta}^3 &= \nu \exp\{(-5E(1-2\delta' - c_B^\alpha) + \Delta_A + 6c_A^\beta \Delta_A + c_B^\alpha \Delta_B)/kT\}, \\
w_{1\alpha}^3 &= \nu \exp\{(-5E(1-2\delta' - c_A^\beta) + \Delta_B + 6c_B^\alpha \Delta_B + c_A^\beta \Delta_A)/kT\}, \\
w_{1\beta}^2 &= \nu \exp\{(-5E(1-2\delta' - c_B^\alpha) + 7c_A^\beta \Delta_A + c_B^\alpha \Delta_B)/kT\}, \\
w_{1\alpha}^2 &= \nu \exp\{(-5E(1-2\delta' - c_A^\beta) + 7c_B^\alpha \Delta_B + c_A^\beta \Delta_A)/kT\}, \\
w_{1\beta}^1 &= \nu \exp\{(-6E(1-2\delta' + c_A^\beta) + \Delta_A + 7c_A^\beta \Delta_A + 2\delta' \Delta_B)/kT\}, \\
w_{1\alpha}^1 &= \nu \exp\{(-6E(1-2\delta' + c_B^\alpha) + \Delta_B + 7c_B^\alpha \Delta_B + \delta' \Delta_A)/kT\},
\end{aligned} \tag{9}$$

where ν is the attempt frequency (for the sake of simplicity in the expressions given here we have assumed that all atoms have the same attempt frequency).

The tracer correlation factor component of the tracer diffusion coefficient is written as

$$\begin{aligned}
f_B &= \frac{\exp\{(-7c_B^\alpha \Delta_B + c_A^\beta \Delta_A - c_B^\alpha c_A^\beta E)/kT\}}{1 - c_A^\beta} \\
&\quad \times \left[4(1 - 23\delta') \left(\frac{w_{0\beta} c_A^\beta}{1 - c_B^\alpha} \exp\{8(1 - 2\delta) \Delta_A/kT\} + 2w_{0\alpha} \right) \right. \\
&\quad + c_B^\alpha [14w_{1\alpha}^3 + 25(w_{1\alpha}^1 + w_{1\alpha}^2)] + \frac{24.1(c_A^\beta/2)^2}{1 - c_B^\alpha} \\
&\quad \left. \times [w_{1\beta}^3 + 1.5(w_{1\beta}^1 + w_{1\beta}^2)] \exp\{8(1 - 2\delta) \Delta_A/kT\} \right]. \tag{10}
\end{aligned}$$

The corresponding expression for the tracer diffusion coefficient of the A component is found by simply interchanging B with A in these expressions as appropriate:

$$\begin{aligned}
D_{A^*} &= \frac{a^2 \exp\{7E_{AB}/kT\}}{2c_A} (8(1 - 23\delta')(2w_{0\beta} c_B^\beta + w_{0\alpha} c_A^\alpha) \\
&\quad + 2c_A^\beta c_B^\beta [14w_{1\beta}^3 + 25(w_{1\beta}^1 + w_{1\beta}^2)] + 24.1c_B^\alpha c_A^\alpha [w_{1\alpha}^3 + 1.5(w_{1\alpha}^1 + w_{1\alpha}^2)]/2) \tag{11}
\end{aligned}$$

$$\begin{aligned}
f_A &= \frac{\exp\{(-7c_A^\beta \Delta_B + c_B^\alpha \Delta_A - c_B^\alpha c_A^\beta E)/kT\}}{1 - c_B^\alpha} \\
&\quad \times \left[4(1 - 23\delta') \left(\frac{w_{0\alpha} c_B^\alpha}{1 - c_A^\beta} \exp\{8(1 - 2\delta) \Delta_B/kT\} + 2w_{0\beta} \right) \right. \\
&\quad + c_A^\beta [14w_{1\beta}^3 + 25(w_{1\beta}^1 + w_{1\beta}^2)] \\
&\quad \left. + \frac{24.1(c_B^\alpha/2)^2}{1 - c_A^\beta} [w_{1\alpha}^3 + 1.5(w_{1\alpha}^1 + w_{1\alpha}^2)] \exp\{8(1 - 2\delta) \Delta_B/kT\} \right]. \tag{12}
\end{aligned}$$

2.4. Phenomenological coefficients

We subdivide the phenomenological coefficients L_{ij} in an entirely analogous way to the tracer diffusion coefficients:

$$L_{AA} = L_{AA}^{\beta-6JC,1} + L_{AA}^{\beta-6JC,2} + L_{AA}^{\alpha-6JC,1} + L_{AA}^{\alpha-6JC,2}, \tag{13}$$

$$L_{BB} = L_{BB}^{\beta-6JC,1} + L_{BB}^{\beta-6JC,2} + L_{BB}^{\alpha-6JC,1} + L_{BB}^{\alpha-6JC,2}, \tag{14}$$

$$L_{AB} = L_{AB}^{\beta-6JC,1} + L_{AB}^{\beta-6JC,2} + L_{AB}^{\alpha-6JC,1} + L_{AB}^{\alpha-6JC,2}. \quad (15)$$

For reasons given by Belova and Murch (2002b) some of the components of the L_{ij} are zero: those identified are $L_{AA}^{\beta-6JC,2}$, $L_{AB}^{\beta-6JC,2}$ and $L_{BB}^{\alpha-6JC,2}$, $L_{AB}^{\alpha-6JC,2}$. Furthermore, several of the components of the L_{ij} are *uncorrelated*¹ and can be written down by inspection: these are

$$L_{BB}^{\beta-6JC,2} = a^2 \frac{N}{kT} c_B^\beta c_v^\beta w_{0\beta}, \quad (16)$$

$$L_{AA}^{\alpha-6JC,2} = a^2 \frac{N}{kT} c_A^\alpha c_v^\alpha w_{0\alpha}, \quad (17)$$

where N is the number of sites per unit volume.

For the remaining components of the L_{ij} we modify, as appropriate, the expressions obtained by Belova and Murch (2002a). These are

$$L_{AA}^{\beta-6JC,1} = Nc_A^\beta (w_{1\beta}^3 + 4.3(w_{1\beta}^1 + w_{1\beta}^2) + 22.5w_{0\beta})c_v^\beta a^2/kT, \quad (18)$$

$$L_{AA}^{\alpha-6JC,1} = Nc_B^\alpha (2w_{1\alpha}^3 + 3(w_{1\alpha}^1 + w_{1\alpha}^2) + w_{0\alpha})c_v^\alpha a^2/kT, \quad (19)$$

$$L_{BB}^{\beta-6JC,1} = Nc_A^\beta (2w_{1\beta}^3 + 3(w_{1\beta}^1 + w_{1\beta}^2) + w_{0\beta})c_v^\beta a^2/kT, \quad (20)$$

$$L_{BB}^{\alpha-6JC,1} = Nc_B^\alpha (w_{1\alpha}^3 + 4.3(w_{1\alpha}^1 + w_{1\alpha}^2) + 22.5w_{0\alpha})c_v^\alpha a^2/kT \quad (21)$$

$$L_{AB}^{\beta-6JC,1} = -2Nc_A^\beta (2w_{1\beta}^3 + 3(w_{1\beta}^1 + w_{1\beta}^2))c_v^\beta a^2/kT \quad (22)$$

$$L_{AB}^{\alpha-6JC,1} = -2Nc_B^\alpha (2w_{1\alpha}^3 + 3(w_{1\alpha}^1 + w_{1\alpha}^2))c_v^\alpha a^2/kT. \quad (23)$$

Now, we can derive expressions for the collective correlation factors (the correlated parts of the corresponding phenomenological coefficients; these quantities are discussed by, for example, Allnatt and Allnatt (1984) and Murch and Qin (1994)):

$$\begin{aligned} f_{AA} = & \frac{c_B^\alpha \exp\{(8\Delta_B - 7c_B^\alpha \Delta_B)/kT\}}{(1 - c_B^\alpha)(1 - c_A^\beta)} [2c_B^\alpha (2w_{1\alpha}^3 + 3(w_{1\alpha}^1 + w_{1\alpha}^2))] \\ & + \frac{2c_A^\beta \exp\{(c_B^\alpha \Delta_B - 7c_A^\beta \Delta_A)/kT\}}{(1 - c_B^\alpha)} [w_{1\beta}^3 + 4.3(w_{1\beta}^1 + w_{1\beta}^2)] \\ & + 5(1 - 23\delta)w_{0\alpha} \exp\{(-8\Delta_A + c_A^\beta \Delta_A + c_B^\alpha \Delta_B + 8c_B^\alpha \Delta_A)/kT\}/c_A^\beta, \end{aligned} \quad (24)$$

$$\begin{aligned} f_{BB} = & \frac{c_A^\beta \exp\{(8\Delta_A - 7c_A^\beta \Delta_A)/kT\}}{(1 - c_B^\alpha)(1 - c_A^\beta)} [2c_A^\beta (2w_{1\beta}^3 + 3(w_{1\beta}^1 + w_{1\beta}^2))] \\ & + \frac{2c_B^\alpha \exp\{(c_A^\beta \Delta_A - 7c_B^\alpha \Delta_B)/kT\}}{(1 - c_A^\beta)} [w_{1\alpha}^3 + 4.3(w_{1\alpha}^1 + w_{1\alpha}^2)] \\ & + 5(1 - 23\delta)w_{0\beta} \exp\{(-8\Delta_B + c_A^\beta \Delta_A + c_B^\alpha \Delta_B + 8c_A^\beta \Delta_B)/kT\}/c_B^\alpha, \end{aligned} \quad (25)$$

$$\begin{aligned} f_{AB}^{(A)} = & -\frac{2(c_B^\alpha)^2 \exp\{(8\Delta_B(1 - 2\delta') + c_B^\alpha \Delta_B - 7c_A^\beta \Delta_A)/kT\}}{(1 - c_B^\alpha)(1 - c_A^\beta)} [2w_{1\alpha}^3 + 3(w_{1\alpha}^1 + w_{1\alpha}^2)] \\ & - \frac{2c_A^\beta \exp\{(c_B^\alpha \Delta_B - 7c_A^\beta \Delta_A - c_B^\alpha c_A^\beta E)/kT\}}{(1 - c_B^\alpha)} [2w_{1\beta}^3 + 3(w_{1\beta}^1 + w_{1\beta}^2)], \end{aligned} \quad (26)$$

¹ This means that the correlated part of the phenomenological coefficient, as reflected by the diagonal collective correlation factor, is unity (Allnatt and Allnatt 1984, Murch and Qin 1994).

$$f_{AB}^{(B)} = -\frac{2(c_A^\beta)^2 \exp\{(8\Delta_A(1-2\delta') + c_A^\beta \Delta_A - 7c_B^\alpha \Delta_B)/kT\}}{(1-c_B^\alpha)(1-c_A^\beta)} [2w_{1\beta}^3 + 3(w_{1\beta}^1 + w_{1\beta}^2)] \\ - \frac{2c_B^\alpha \exp\{(c_A^\beta \Delta_A - 7c_B^\alpha \Delta_B - c_B^\alpha c_A^\beta E)/kT\}}{(1-c_A^\beta)} [2w_{1\alpha}^3 + 3(w_{1\alpha}^1 + w_{1\alpha}^2)]. \quad (27)$$

2.5. Thermodynamic factor

In order to obtain expressions for the intrinsic diffusion and interdiffusion coefficients we first need to have an appropriate expression for the thermodynamic factor. Here we calculate the thermodynamic factor at the Bragg–Williams approximation but using a far simpler procedure than that used by Chang and Neumann (1982) and Ikeda *et al* (1998) in their calculations.

The thermodynamic factor ϕ is usually written in the well known form

$$\phi = 1 + \frac{\partial \ln \gamma_A}{\partial \ln c_A} = 1 + \frac{\partial \ln \gamma_B}{\partial \ln c_B}, \quad (28)$$

where $\gamma_{A(B)}$ is the activity coefficient of A (B). Equivalently, in the binary system the thermodynamic factor can be expressed as

$$\phi = \frac{1}{kT c_A c_B} \frac{\partial(\mu_A - \mu_B)}{\partial c_A}, \quad (29)$$

where $\mu_{A(B)}$ are the chemical potentials of A (B). We now make use of the exact expression for the difference in chemical potentials $\mu_A - \mu_B$ provided by Belova and Murch (1996b) for the ordered alloy. The expression was based on the application to binary systems of the powerful ‘potential distribution method’ of Widom (1963):

$$\mu_A - \mu_B = -kT \ln \left(\frac{c_B^\alpha \exp(-(E_A^\alpha - E_B^\alpha)/kT) + c_B^\beta \exp(-(E_A^\beta - E_B^\beta)/kT)}{2c_A} \right), \quad (30)$$

where E_A^α is the average energy (arising from interactions) of an A atom on the α sublattice and the other quantities are defined by analogy.

Assuming a *random* distribution of antistructural atoms on each sublattice (Bragg–Williams approximation) we can immediately rewrite this equation as

$$\mu_A - \mu_B = -kT \ln \left(\frac{c_B^\alpha}{c_A^\alpha} \right) + E_A^\alpha - E_B^\alpha. \quad (31)$$

Using equations (2) we can write that

$$\frac{\partial c_A^\alpha}{\partial c_A} = -\frac{\partial c_B^\alpha}{\partial c_A}; \quad \frac{\partial c_B^\beta}{\partial c_A} = -2 - \frac{\partial c_B^\alpha}{\partial c_A}; \quad \frac{\partial c_A^\beta}{\partial c_A} = 2 + \frac{\partial c_B^\alpha}{\partial c_A}. \quad (32)$$

From equation (3) we then have that

$$\frac{\partial c_B^\alpha}{\partial c_A} = \left(\frac{16E}{kT} - \frac{2}{c_A^\beta c_B^\beta} \right) \left(-\frac{16E}{kT} + \frac{1}{c_A^\alpha c_B^\alpha} + \frac{1}{c_A^\beta c_B^\beta} \right)^{-1}. \quad (33)$$

The final expression for the thermodynamic factor is

$$\phi = \frac{8}{kT} c_A c_B E \left(2 + \frac{\partial c_B^\alpha}{\partial c_A} \right) - \frac{c_A c_B}{c_A^\alpha c_B^\alpha} \left(\frac{\partial c_B^\alpha}{\partial c_A} \right) \quad (34)$$

where $\partial c_B^\alpha / \partial c_A$ is given by equation (33).

For the intermetallic, equation (34) produces a (symmetric) maximum precisely at the stoichiometric composition. This well known behaviour has been demonstrated by computer simulation (Zhang *et al* 1988) and has been observed in a large number of experimental systems

(see the review by Chang and Neumann (1982)). If the experimental thermodynamic factor is not quite symmetric about the stoichiometric composition, it implies either composition-dependent interaction energies or other defects participating in the disorder, e.g. structural vacancies.

2.6. Intrinsic and interdiffusion coefficients

The intrinsic diffusion coefficients of the components A and B can be expressed in terms of the L_{ij} in the usual way as

$$D_A^I = \phi \frac{kT}{N} \left(\frac{L_{AA}}{c_A} - \frac{L_{AB}}{c_B} \right); \quad D_B^I = \phi \frac{kT}{N} \left(\frac{L_{BB}}{c_B} - \frac{L_{AB}}{c_A} \right). \quad (35)$$

For the interdiffusion coefficient we have that

$$\tilde{D} = c_A D_B^I + c_B D_A^I \quad (36)$$

and therefore that

$$\tilde{D} = \phi \frac{kT}{N} \left(\frac{c_B L_{AA}}{c_A} + \frac{c_A L_{BB}}{c_B} - 2L_{AB} \right). \quad (37)$$

The intrinsic diffusion coefficients and the interdiffusion coefficient can therefore be readily obtained using the expressions for the phenomenological coefficients and thermodynamic factor given above.

The Darken–Manning expression (Darken 1948, Manning 1968) relates the interdiffusion coefficient, the tracer diffusion coefficients and the thermodynamic factor:

$$\tilde{D} = \phi S (c_A D_{B^*} + c_B D_{A^*}), \quad (38)$$

where S is the vacancy-wind factor (sometimes called the Manning factor) and is given by the exact expression

$$S = \frac{kT}{N} \left(\frac{c_B^2 L_{AA} + c_A^2 L_{BB} - 2c_B c_A L_{AB}}{c_B c_A (c_A D_{B^*} + c_B D_{A^*})} \right) = \frac{c_B f_{AA} + c_A g f_{BB} - 2c_A f_{AB}^{(A)}}{c_B f_A + c_A g f_B}, \quad (39)$$

where g is the ratio of the numbers of B atom jumps per atom to A atom jumps per atom. In the present case g is given by

$$g = \frac{c_A c_B^\alpha}{c_B c_A^\alpha} \exp\{8(\Delta_B - c_A^\beta E)/kT\}. \quad (40)$$

Equation (39) can be used to calculate the vacancy-wind factor in the present formalism.

Manning's (1968, 1971) well known approximate expression for S is one of the products of his diffusion kinetics formalism for the random alloy:

$$\begin{aligned} S &= 1 + \frac{1 - f_0}{f_0} \frac{c_A c_B (D_{A^*} - D_{B^*})^2}{(c_A D_{A^*} + c_B D_{B^*})(c_A D_{B^*} + c_B D_{A^*})} \\ &= 1 + \frac{1 - f_0}{f_0} \frac{c_A c_B (g f_B - f_A)^2}{(c_A f_A + c_B g f_B)(c_A g f_B + c_B f_A)}, \end{aligned} \quad (41)$$

where f_0 is the geometric tracer correlation factor for the structure; in this case $f_0 = 0.72722$ (b.c.c.).

It has been shown by Belova and Murch (2001) that equation (41) is not accurate at low temperatures at the stoichiometric composition where the 6JCs clearly operate. For diffusion by pure 6JCs at the stoichiometric composition it is readily shown that S takes the value of 0.42 for the B2 structure (Belova and Murch 2001). For reference purposes the vacancy-wind factor according to equation (41) can be calculated in the present formalism.

2.7. Computer simulation

It is generally accepted, see, for example, Bakker (1984) and Murch (1984), that in intermetallics the Bragg–Williams approximation provides a very good description of the average jump frequencies and thermodynamic factor except in the vicinity of the order–disorder temperature (the value of which is poorly described by this approximation). The reason for the success of the Bragg–Williams approximation is simply a result of the relatively small population of antistructural atoms, which are essentially randomly distributed. The searching test of the present diffusion kinetics theory is the determination of the correlation factors, these being the tracer correlation factors, the collective correlation factors and their combination to form the vacancy-wind factor S via equation (39). Computer simulation of these factors was performed using standard procedures described, for example, by Belova and Murch (1996b, 2000a). (The interested reader is also directed to an older review on Monte Carlo simulation of diffusion kinetics by Murch (1984).) All the computer simulations here made use of single vacancy jumps; in other words, the 6JC was *not* explicitly specified in the simulations.

The periodic cell used in the present calculations was $100 \times 100 \times 100$ (which means that we had 125 000 sites on each sub-lattice). For the tracer correlation factor we specified 200 jumps per atom (more jumps did not change the results). Collective correlation factors were calculated using 100 000 observations with the number of vacancy jumps in each observation sufficiently large to provide at least 2000 jumps per atomic species.

3. Results and discussion

In figures 2(a) and (b) we present analytical and Monte Carlo results for the tracer correlation factors f_A and f_B (equations (10) and (12)) as a function of composition c_A for the conditions $E/kT = 1.6$ and $U = 0.0, +0.125$ (the case when $U = -0.125$ can be obtained from the case $U = +0.125$ by interchanging A and B). This temperature is approximately 0.39 of the order–disorder temperature. At this temperature and at the stoichiometric composition the value of $c_A^B (=c_B^A$ at stoichiometry with a low vacancy content) was found to equal 0.0017. For a cell of the size of 250 000 sites in total this antistructural atom population means that we had about 200 each of the two types of antistructural atom at the stoichiometric composition.

It can be seen that there is excellent agreement between the analytical results describing diffusion by 6JCs and the results of the simulations describing diffusion only by single vacancy jumps. The very low values taken by the correlation factors should be noted. This is a natural result of many jumps of individual atoms from their home sublattice to the other sublattice being immediately reversed. In the context of the 6JC it means that many such jump reversals punctuate a given cycle. We might mention here that in general, as U increases, one tracer correlation factor remains small whilst the other approaches values of the order of unity.

In figures 3(a) and (b) we present corresponding results for the diagonal collective correlation factors f_{AA} and f_{BB} (equations (24) and (25)) for the same conditions as above for the tracer correlation factors. Again there is seen to be excellent agreement between theory and simulation. The very small values of the correlation factors are again a result of the frequent jump reversals discussed above.

In figures 4(a) and (b) we present corresponding results for the off-diagonal collective correlation factors $f_{AB}^{(i)}$ $i = A, B$ (equations (26) and (27)). Again there is excellent agreement with computer simulations. It should be noted that these correlation factors are very small but also negative. For diffusion by *pure* 6JCs in the perfectly ordered structure at the stoichiometric composition it is easily shown that the off-diagonal collective correlation factors are zero (Belova and Murch 2001). The small antistructural atom population in conjunction with the

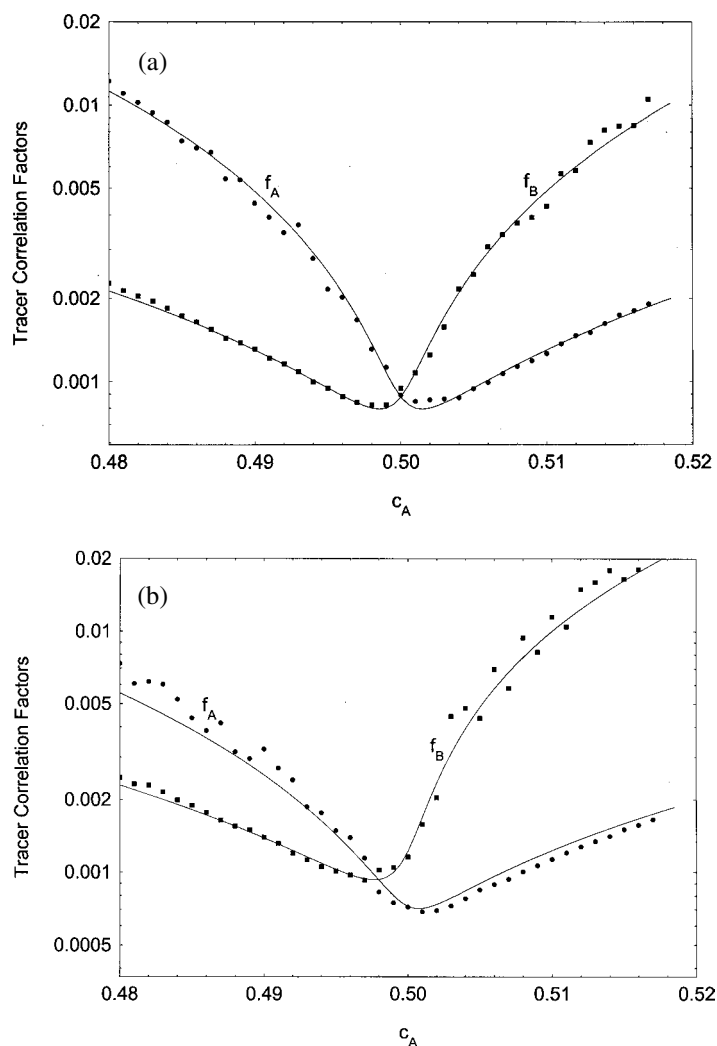


Figure 2. The tracer correlation factors f_A and f_B as a function of composition c_A for the conditions $E/kT = 1.6$ and (a) $U = 0.0$, (b) $U = +0.125$. Solid curves, equations (10), (12); symbols, computer simulation results.

frequency relationships given by equation (6) inevitably gives negative cross-correlation factors in an entirely analogous way to that found for the five-frequency model for impurity diffusion (see for example, Allnatt 1981a, 1981b).

In figures 5(a) and (b) we present corresponding results for the vacancy-wind factor S as featured in equation (39). As mentioned in section 2.6 the vacancy-wind factor for interdiffusion by pure 6JCs at the stoichiometric composition with perfect order in the B2 structure takes a value of 0.42 (Belova and Murch 2001). This provides a very useful lower limit. There is a reasonable amount of scatter in the data points because of the great magnification of errors. Nonetheless it is quite clear that the analytical results generally follow the simulation data very well. For reference purposes we also include the Manning (1968, 1971) result for S (equation (41)). It is clear that this gives values for S that are systematically

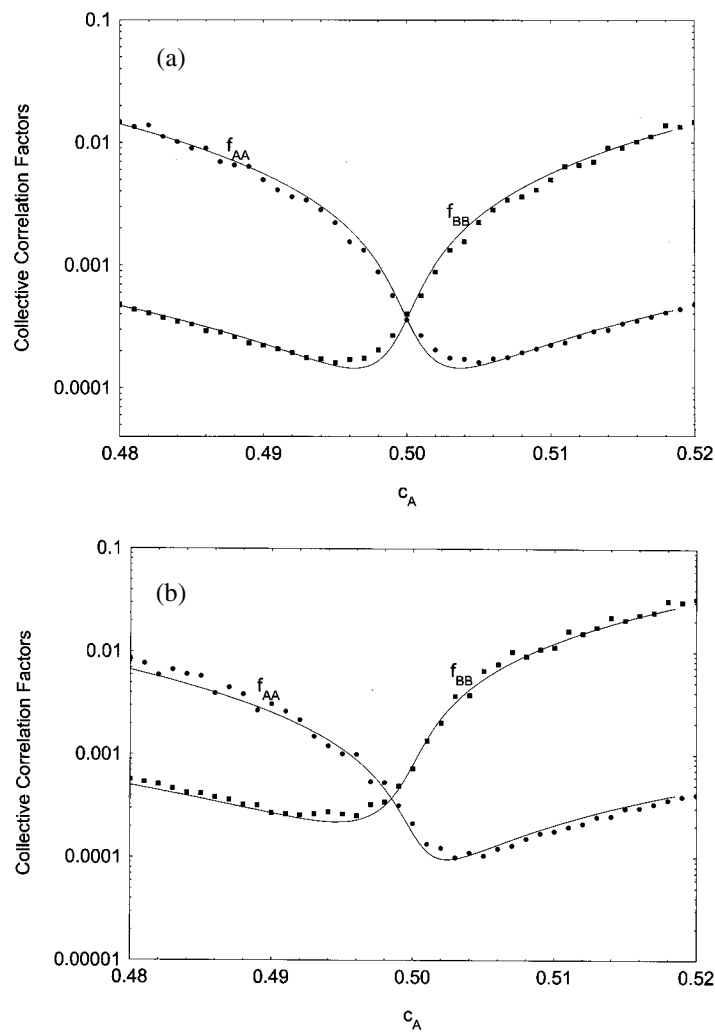


Figure 3. The diagonal collective correlation factors f_{AA} and f_{BB} as a function of composition c_A for the conditions $E/kT = 1.6$ and (a) $U = 0.0$, (b) $U = +0.125$. Solid curves, equations (24), (25); symbols, computer simulation results.

higher by roughly a factor of 2.4. We emphasize however that at temperatures closer to the order–disorder temperature where the 6JC no longer dominates diffusion the Manning expression becomes acceptable (see also Belova and Murch 1997, 2001).

It is well known that the pure 6JC gives limits of roughly 0.5 and 2.0 for the ratio of the tracer diffusion coefficients. These limits have been widened further recently in a re-analysis of the 6JC (Drautz and Fahnle 1999). A Monte Carlo study using a four-frequency model showed that the limits widen greatly with even a small population of intrinsic antistructural atoms (Belova and Murch 1999). Similar behaviour can be expected from the present formalism. Furthermore, extrinsic antistructural atoms will give analogous behaviour. Accordingly, from a purely practical point of view, comparison of the measured *ratio* of the tracer diffusion coefficients with limits for the 6JC is unlikely to be rewarding.

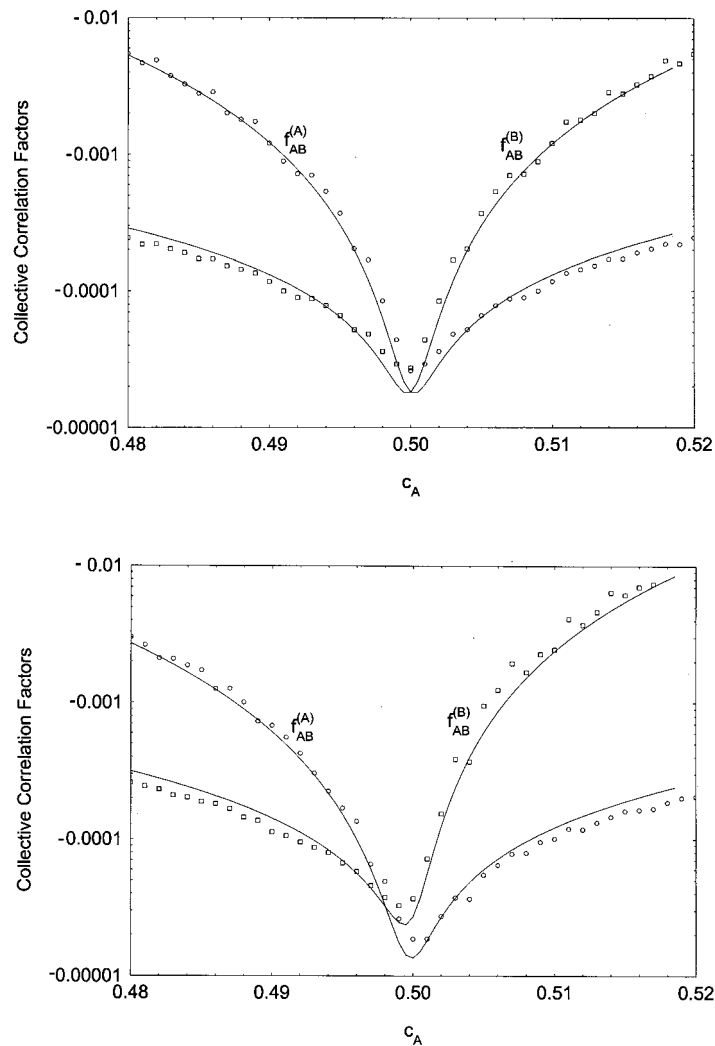


Figure 4. The off-diagonal collective correlation factors $f_{AB}^{(A)}$ and $f_{AB}^{(B)}$ as a function of composition c_A for the conditions $E/kT = 1.6$ and (a) $U = 0.0$, (b) $U = +0.125$. Solid curves, equations (26), (27); symbols, computer simulation results.

4. Conclusions

In this paper we have formulated a comprehensive diffusion kinetics theory to describe seamlessly tracer and chemical diffusion in antistructurally disordered B2 intermetallics exhibiting positive and negative deviations from stoichiometry. The theory was based around unit processes consisting of 6JCs that can be assisted by intrinsic and extrinsic antistructural atoms of either atomic species. The Ising alloy model was used to illustrate the formalism, but the formalism can be adapted to other models. Analytical expressions were developed for the tracer diffusion coefficients, the phenomenological coefficients, the intrinsic diffusion coefficients, the interdiffusion coefficient and the various correlation factor components. There was excellent agreement between the results of the formalism and Monte Carlo computer

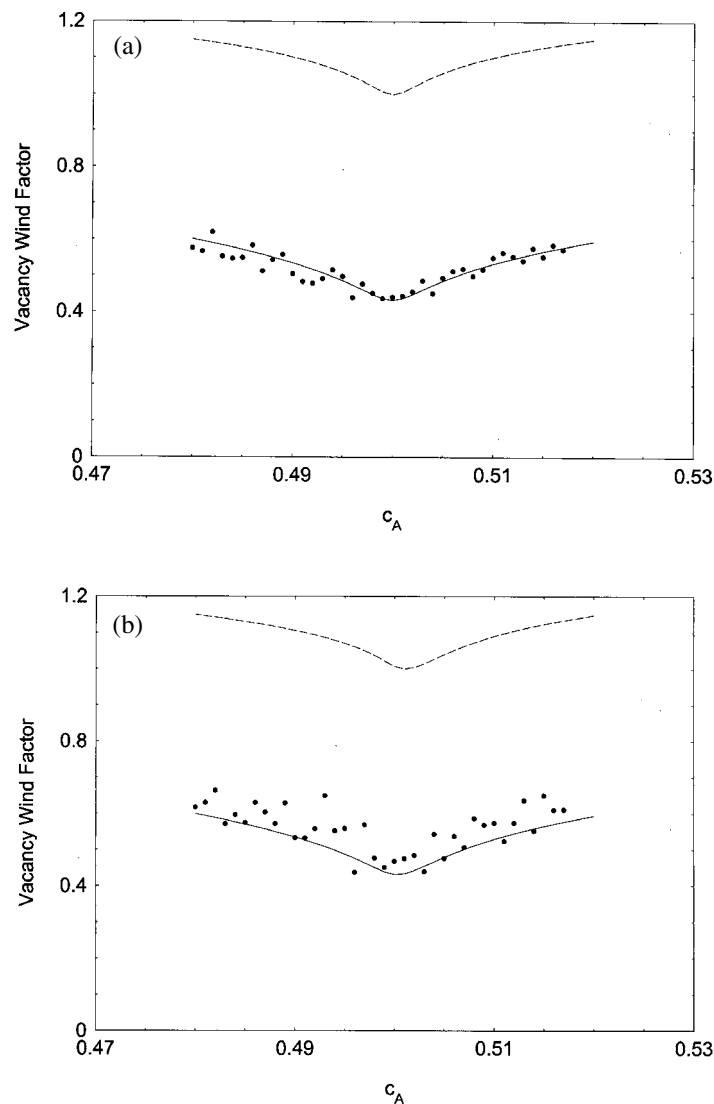


Figure 5. The vacancy-wind factor S as a function of composition c_A for the conditions $E/kT = 1.6$ and (a) $U = 0.0$, (b) $U = +0.125$. Solid curve, equation (39); dashed curve, equation (41); symbols, computer simulation results.

simulation results based on *single* vacancy jumps. This agreement strongly suggests that the physics of the diffusion process in this type of highly ordered structure is quantitatively very well captured in the present analysis.

Acknowledgments

We wish to thank the Australian Research Council (Large Grants and Discovery Project Grants Schemes) for its support of this research. One of us (IVB) also wishes to thank the Australian Research Council for the award of a Queen Elizabeth II Fellowship.

References

- Allnatt A R 1981a *J. Phys. C: Solid State Phys.* **14** 5453
Allnatt A R 1981b *J. Phys. C: Solid State Phys.* **14** 5467
Allnatt A R and Allnatt E L 1984 *Phil. Mag.* A **49** 625
Allnatt A R and Lidiard A B 1993 *Atomic Transport in Solids* (Cambridge: Cambridge University Press)
Arnhold V 1981 *Thesis* Westfälische Wilhelms Universität, Münster
Athènes M, Bellon P and Martin G 1997 *Phil. Mag.* A **76** 965
Bakker H 1984 *Diffusion in Crystalline Solids* ed G E Murch and A S Nowick (Orlando, FL: Academic) p 189
Bakker H, Stolwijk N A, Van der Meij L and Zuurendonk T J 1976 *Nucl. Metall.* **20** 96
Belova I V, Ivory M E and Murch G E 1995 *Phil. Mag.* A **72** 871
Belova I V and Murch G E 1996a *Phil. Mag.* A **73** 117
Belova I V and Murch G E 1996b *Phil. Mag.* A **73** 1699
Belova I V and Murch G E 1997 *Phil. Mag.* A **75** 1715
Belova I V and Murch G E 1998 *Acta Mater.* **46** 849
Belova I V and Murch G E 1999 *Phil. Mag.* A **79** 193
Belova I V and Murch G E 2000a *J. Phys. Chem. Solids* **61** 1755
Belova I V and Murch G E 2000b *Phil. Mag.* A **80** 1481
Belova I V and Murch G E 2001 *Phil. Mag.* A **81** 83
Belova I V and Murch G E 2002a *Phil. Mag.* A **82** 269
Belova I V and Murch G E 2002b *Phil. Mag.* A **82** 285
Chang Y A and Neumann J P 1982 *Prog. Solid State Chem.* **14** 221
Darken L S 1948 *Trans. AIME* **175** 184
Domian H A and Aaronson H I 1964 *Trans. TMS: AIME* **230** 44
Domian H A and Aaronson H I 1965 *Diffusion in Body Centred Cubic Metals* ed J A Wheeler and F R Winslow (Metals Park, OH: ASM) p 209
Drautz R and Fahnle M 1999 *Acta Mater.* **47** 2437
Elcock E W and McCombie C W 1958 *Phys. Rev.* **109** 605
Ikeda T, Numukara H and Koiwa M 1998 *Acta Mater.* **46** 6605
Manning J R 1968 *Diffusion Kinetics for Atoms in Crystals* (Princeton, NJ: Van Nostrand-Reinhold)
Manning J R 1971 *Phys. Rev.* B **4** 1111
Mishin Y and Farkas D 1997 *Phil. Mag.* A **75** 187
Murch G E 1984 *Diffusion in Crystalline Solids* ed G E Murch and A S Nowick (Orlando, FL: Academic) p 379
Murch G E and Belova I V 1998 *Proc. Mater. Res. Soc.* **527** 81
Murch G E and Qin Z 1994 *Defect Diffus. Forum* **109** 1
Murch G E and Thorn R J 1978 *J. Nucl. Mater.* **11** 219
Widom B 1963 *J. Chem. Phys.* **39** 2808
Zhang L, Oates W A and Murch G E 1988 *Phil. Mag.* A **58** 937