Vacancy-Wind Factors and Collective Correlation Factors in Nonstoichiometric B2 Intermetallic Compounds

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Abstract. The six-jump-cycle (6JC) diffusion mechanism is used to analyze the behavior of vacancy-wind factors and collective correlation factors in partially ordered B2 intermetallic compounds at stoichiometric and near- stoichiometric compositions. Expressions for the vacancy-wind factors are obtained in the framework of the four-frequency model where the two sublattices exist *a priori*. The phenomenological coefficients on the two sublattices that remain hitherto independent in 6JC mechanism are connected through a microscopic detailed balance condition. The present results for collective correlation factors when compared with our earlier calculation based on taking the harmonic mean of the sublattice correlation factors show much better agreement with Monte Carlo simulation results. The collective correlation factors and tracer correlation factors are used to calculate the vacancy-wind factors. Our results for vacancy-wind factors agree qualitatively with the simulation data when the frequency ratio (α) of structural and antistructural atoms jumps decreases up to the order of unity.

Introduction

The vacancy-wind effect [1-4] occurs when a collective diffusion process such as chemical diffusion (or ionic conductivity) causes a net flux of vacancies which is then distorted around a tracer atom causing non-random jumping of that tracer atom. The vacancy-wind effect is embodied in expressions for intrinsic diffusivities and interdiffusivities in the form of vacancy-wind factors [5-6].

The vacancy-wind factors can be expressed *exactly* in terms of the tracer and collective correlation factors as, see refs. [7-8]:

$$r_A = \frac{(f_{AA} - C_A C_B^{-1} f_{AB}^{(A)})}{f_A} \quad (1)$$

$$r_B = \frac{(f_{BB} - C_B C_A^{-1} f_{AB}^{(B)})}{f_B} \quad (2)$$

$$S = \frac{C_B f_{AA} + C_A g f_{BB} - 2 C_A g f_{AB}^{(A)}}{C_A g f_B + C_B f_A} \quad (3)$$

where r_A and r_B are respectively the vacancy-wind factors for atoms of type A and B that occur in the intrinsic diffusivities and S is the vacancy-wind factor occurring in the interdiffusivity, f_A and f_B are the tracer correlation factors for A and B atoms respectively, f_{AA} , f_{BB} , $f_{AB}^{(A)}$ and $f_{AB}^{(B)}$ are the collective correlation factors and $C_{A(B)}$ is the site fraction of atoms A(B) and g is given by:

$$g = \frac{C_A}{C_B} \left(\frac{L_{BB}^{(0)}}{L_{AA}^{(0)}} \right) \quad (4)$$

where $L^{(0)}$ are the uncorrelated parts of the phenomenological coefficients.

In the present paper, our aim is to investigate the experimentally accessible vacancy-wind factors and collective correlation factors [9-10] for partially ordered B2 intermetallic compound and at small deviations from the stoichiometric composition. Recently, expressions for tracer and collective correlation factors were obtained by us [11-12] for B2 intermetallic compound using the well known six-jump-cycle (6JC) mechanism of diffusion. The correlation factors were calculated by taking harmonic mean of the sublattice correlation factors, since the dynamics of the two sublattices remain independent of each other. In the present work we obtain the phenomenological coefficients for the system by connecting the expressions of sublattice phenomenological coefficients through the condition of detailed-balance. These collective correlation factors and the tracer correlation factors obtained earlier [11] are assembled to calculate the vacancy-wind factors.

The Four-Frequency Model and the 6JC-frequency

We consider an AB intermetallic compound where sublattice-1 constitutes the home sublattice of atoms of type B and sublattice-2 is the home sublattice of atoms of type A [13-14]. For two different kinds of vacancies, denoted as V1 and V2 on sublattices- 1 and 2 respectively, there are four nearest-neighbour atom-vacancy exchange frequencies. For example, W_{A1} denotes the jump frequency when an A atom on sublattice-1 exchanges its position with a vacancy V2 on sublattice-2. Similarly, we define W_{B1} , W_{A2} and W_{B2} . In a nonstoichiometric compound, we consider the 6JC as a fundamental unit of diffusion for the cycle involving structural atoms, and the two-jump-cycle (2JC) as a fundamental unit for the cycle involving antistructural atom at the [110]-type or [100]-type sites. The average jump frequency of a single isolated 6JC for a fully ordered configuration can be obtained as [11-12]:

$$v_{B1} \equiv v_{A2} = \frac{\alpha^3 (3 + 6\alpha + 4\alpha^2)}{(288 + 1152\alpha + 2232\alpha^2 + 2325\alpha^3 + 1360\alpha^4 + 364\alpha^5 + 48\alpha^6 + 4\alpha^7)} \quad (5)$$

where α is the ratio of jump frequencies of atoms going from the 'right' to the 'wrong' sublattice to that from the 'wrong' to 'right' sublattice:

$$\alpha = \frac{W_{B1}}{W_{B2}} = \frac{W_{A2}}{W_{A1}} \quad (6)$$

The average jump frequency of a single isolated 2JC for the antistructural atom can be written as [14]:

$$v_{A1} \equiv v_{B2} = \frac{2\alpha}{(1+\alpha)} \quad (7)$$

Tracer correlation Factors

In an earlier paper [11], using the 6JC mechanism we have obtained the tracer correlation factors when the frequencies of [110]-cycle, [100]-straight and [100]-bent cycles were taken to be equal. The tracer correlation factors for sublattice-1 are expressed as:

$$f_{T1} = 1 - \frac{v_{T1}}{3} \left[\frac{(2J' + J)(b'_{T1} - 2b_{T1}) - (2J'' + J')(a'_{T1} - 2a_{T1})}{(a_{T1}b'_{T1} - a'_{T1}b_{T1})} \right] \quad (8)$$

where

$$a_{T1} = \left(1 - \frac{J}{2}\right) v_{V1} + v_{T1} J \quad ; \quad a'_{T1} = -(v_{V1} - 2v_{T1}) J' \quad (9a)$$

$$b_{T1} = -\frac{1}{2}(v_{V1} - 2v_{T1}) J' \quad ; \quad b'_{T1} = (1 - J'') v_{V1} + 2v_{T1} J'' \quad (9b)$$

and

$$v_{V1} = C_{A1} v_{A1} + C_{B1} v_{B1} \quad (9c)$$

where v_{V1} is the vacancy escape frequency on sublattice-1. The f_{T2} can be obtained from the above equations by changing the subscript 1 as 2. Here $v_{T1(2)}$ is 6JC frequency of the tracer, which is equal to that of A and B atoms on sublattice-1(2) when tracer atom T=A, B respectively. The J, J' and J'' are the Brillouin-zone integrals whose values are given by 0.2416, 0.0259 and 0.1253 respectively. The tracer correlation factor f_T is given by the harmonic mean of the sublattice tracer correlation factors [11, 14] as:

$$f_T = 2 \left(\frac{1}{f_{T1}} + \frac{1}{f_{T2}} \right)^{-1} \quad (10)$$

Phenomenological Coefficients and Collective Correlation Factors

The phenomenological transport coefficients L_{ij} ($i, j=A, B$) for an intermetallic compound can be expressed as [15]:

$$L_{ij} = L_{i1j1} + L_{i2j2} + 2L_{i1j2} \quad (11)$$

where L_{i1j1} and L_{i2j2} are respectively the phenomenological coefficients for sublattices-1 and 2 respectively. The Onsager reciprocity condition relates the cross-coefficients $L_{i1j2} = L_{i2j1}$. When diffusion is governed by the 6JC mechanism [16-17], the dynamics on the two sublattices is independent of each other since vacancy on a particular sublattice has no means of switching over to the other sublattice. Consequently, the cross-coefficients vanish and we have that:

$$L_{ij} = L_{i1j1} + L_{i2j2} \quad (12)$$

For the evaluation of the L_{ij} , we follow the general linear response theory of Allnatt and Lidiard [18] and divide it into the uncorrelated and correlated parts. The uncorrelated and correlated parts of the phenomenological coefficients for the sublattice, say sublattice-1, can be obtained as; see [12]:

$$L_{i1j1}^{(0)} = \delta_{ij} \left(\frac{6Na^2}{k_B T} \right) C_{v1} C_{i1} v_{i1} \quad (13)$$

$$L_{i1j1}^{(1)} = (1 - 2\delta_{ij}) \left(\frac{2Na^2}{k_B T} \right) v_{i1} v_{j1} C_{v1} C_{i1} (1 - C_{i1}) \left[\frac{(2J' + J)(b'_1 - 2b_1) - (2J'' + J')(a'_1 - 2a_1)}{(a_1 b'_1 - a'_1 b_1)} \right] \quad (14)$$

where

$$a_1 = \left(1 - \frac{J}{2} \right) v_{v1} + v_1 J \quad ; \quad a'_1 = -(v_{v1} - 2v_1) J' \quad (15a)$$

$$b_1 = -\frac{1}{2} (v_{v1} - 2v_1) J' \quad ; \quad b'_1 = (1 - J'') v_{v1} + 2v_1 J'' \quad (15b)$$

and

$$v_1 = C_{A1} v_{B1} + C_{B1} v_{A1} \quad (15c)$$

Figure 1. Collective correlation factors f_{AA} , f_{BB} , $f_{AB}^{(A)}$, $f_{AB}^{(B)}$ as a function of C_A for $\alpha = 0.1$: (—) Calculated values, (* * *) Simulation results, (-----) harmonic mean method.

Figure 2. Collective correlation factors f_{AA} , f_{BB} , $f_{AB}^{(A)}$, $f_{AB}^{(B)}$ as a function of C_A for $\alpha = 0.08$: (—) Calculated values, (* * *) Simulation results, (-----) harmonic mean method.

Figure 3. Collective correlation factors f_{AA} , f_{BB} , $f_{AB}^{(A)}$, $f_{AB}^{(B)}$ as a function of C_A for $\alpha = 0.06$: (—) Calculated values, (***) Simulation results, (----) harmonic mean method.

Figure 4. Collective correlation factors f_{AA} , f_{BB} , $f_{AB}^{(A)}$, $f_{AB}^{(B)}$ as a function of C_A for $\alpha = 0.04$: (—) Calculated values, (***) Simulation results, (----)harmonic mean method.

Figure 5. Vacancy-wind factor r_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 –present method, dashed line –harmonic mean method.

Figure 6. Vacancy-wind factor r_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 –present method, dashed line –harmonic mean method.

Figure 7. Vacancy-wind factor S 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 – present method, dashed line – harmonic mean method.

Figure 8. Vacancy-wind factors r_A , r_B and S as a function of α at the stoichiometric composition ($C_A = 0.5$) for the B2 intermetallic compound. Solid line: present calculations for $r_A (= r_B = S)$. Symbols: Monte Carlo simulation, * - for r_A ; x -for r_B ; +- for S .

Figure 9. Vacancy-wind factors r_A , r_B and S as a function of α at the non-stoichiometric composition ($C_A=0.48$) for the B2 intermetallic compound. Solid line: present calculations. Symbols: Monte Carlo simulation, * - for r_A ; x -for r_B ; +- for S .

The expressions for the sublattice-2 can be obtained from above by interchanging the subscripts 1 and 2. The phenomenological coefficients L_{ij} are obtained from Eq. 12 by combining the results of the two sublattices using the detailed balance condition given as:

$$\frac{C_{V2}}{C_{V1}} = \left(\frac{C_{A2} C_{B2} W_{A2} W_{B2}}{C_{A1} C_{B1} W_{A1} W_{B1}} \right)^{1/2} \quad (16)$$

The collective correlation factors are then given by:

$$f_{ij}^{(j)} = \delta_{ij} + \frac{L_{ij}^{(1)}}{L_{jj}^{(0)}} \quad (17)$$

The superscript j is omitted when $i=j$.

Results and Discussion

In order to verify the above relations for collective correlation factors, we represent in Figs. 1-4 the f_{ij} as a function of equilibrium composition of A atoms (C_A) at fixed values of jump frequencies ratio $\alpha = 0.1, 0.08, 0.06, 0.04$. The results for collective correlation factors are compared with the results of Monte Carlo simulation based on single vacancy jumps. Results are also compared with our earlier calculation based on the harmonic mean of the sublattice correlation factors. The agreement of the present results with the Monte Carlo simulation data is quite good for diagonal collective correlation factors (f_{AA} and f_{BB}) as compared to off-diagonal ones ($f_{AB}^{(A)} = f_{BA}^{(A)}$ and

$f_{AB}^{(B)} = f_{BA}^{(B)}$ at $\alpha = 0.1$ as shown in Fig. 1. The cross correlation factors are much smaller and are of the order of 10^{-2} . However, all the four correlation factors agree closely with the simulation results at $\alpha = 0.04$ (See Fig. 4).

The results for vacancy-wind factors r_A , r_B and S are shown in Figs. 5, 6 and 7 respectively as a function of C_A at fixed values of jump frequencies ratio $\alpha = 0.9, 0.5, 0.3, 0.1$. The present results for r_A , r_B and S are in much better agreement with the simulated values as compared to that obtained using harmonic mean method. Fig. 8 shows the variation of the vacancy-wind factors r_A ($=r_B=S$) with α at stoichiometry for the symmetric case where asymmetry parameter is unity [19]. At $\alpha = 1$, the distinction between the two sublattices is lost and A behaves exactly the same as B (apart from identity). Under such conditions $D_A^I = D_B^I$ and $r_A = r_B = 1$. This is verified in the Fig. 8. Physically, $D_A^I = D_B^I$ means that there would be no marker shift in the interdiffusion experiment and consequently no net vacancy flux. Without a vacancy flux, there can be no vacancy-wind effect and both r_A and r_B are trivially equal to unity. In Fig. 9 we have shown r_A , r_B and S as a function of α at small deviation from stoichiometry ($C_A=0.48$). The results are qualitatively similar to the simulation data, except that the deviation from the simulation data increases as α decreases.

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