Diffusion Mechanism in Ordered Alloys
—A Detailed Analysis of Six-Jump Vacancy Cycle in a Two-Dimensional Ordered Lattice—

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Atom movements via six-jump vacancy cycle are analysed in detail for a two-dimensional ordered alloy, AB. The diffusion coefficients, $D_A$ and $D_B$, are expressible in terms of the effective jump frequency, $\bar{v}$, for the six-jump vacancy cycle, and the correlation factors, $f_A$ and $f_B$. By applying the theory of stochastic processes, the analytical expression for $\bar{v}$ is derived in terms of six individual jump frequencies of vacancy. The correlation factors, $f_A$ and $f_B$, can be calculated exactly: $f_A = 1/(\sqrt{2} - 1)$, $f_B = \sqrt{2}/(\sqrt{2} + 2)$.

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I. Introduction

The movement of atoms in crystals is known to occur very commonly through site exchanges of atoms with vacancies. In pure metals, self diffusion occurs by the random motion of vacancies. In ordered alloys or intermetallic compounds, in contrast, random vacancy motion would disrupt the ordered arrangement of atoms; some highly correlated motion of vacancies must be occurring in these materials. Huntington(1) first suggested the possibility of a six-jump vacancy cycle, which brings about the long range vacancy migration with minimal temporary disordering. Elcock and McCombie(2) and Elcock(3) have examined, in some detail, such processes for the stoichiometric simple cubic binary alloys. Wynblatt(4) has discussed the relative importance of various mechanisms in the B2(CsCl type) lattice, and concluded that the six-jump vacancy cycle is a favourable mechanism.

Although, in these investigations, the geometrical aspect of the cycle has been analysed in detail, the expression of the diffusion coefficient in terms of individual vacancy jump frequencies has not been derived. The aim of this paper is to derive the analytical expression of the diffusion coefficient for the stoichiometric two-dimensional (square) binary alloy. This investigation was initiated as preliminary to the calculation of the diffusion coefficient in three-dimensional alloys. In a two-dimensional alloy, the problem is greatly simplified, and yet salient points characteristic of the diffusion process in ordered alloys can be demonstrated clearly.

II. Six-jump Vacancy Cycle

Consider a square lattice with the lattice constant $a$, as shown in Fig. 1. The lattice consists of two sublattices, $\alpha$ and $\beta$ (the lattice constant $\sqrt{2}a$); A and B atoms occupy $\alpha$ and $\beta$ sites, respectively. We shall consider the migration of a vacancy initially at an $\alpha$ site.

If we allow only nearest neighbour jumps, the vacancy movement creates wrong bonds, thus increasing the energy of the system. There exist some paths of the vacancy movement which eventually results in exchange of the vacancy with a neighbouring A atom with a minimum increase of energy. Figure 2 illustrates such a series of vacancy jumps. After
the completion of six jumps, the net result is:

(1) an A atom exchanges the position with the vacancy in the same sublattice and
(2) two B atoms which constitute the cycle exchange each other.

The configuration of atoms and the vacancy can be specified by the number of vacancy jumps; the state before the i-th vacancy jump is referred to as C_i (Configuration i). The number of nearest neighbour wrong bonds A-A and B-B for each configuration are listed in Table 1. On the basis of the table, the energy changes taking place during vacancy motion can be schematically depicted, as shown in Fig. 3. The individual jump frequencies of vacancy

| Configuration | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
|---------------|---|---|---|---|---|---|---|
| the number of wrong bonds | A-A | 0 | 0 | 2 | 2 | 2 | 0 | 0 |
| B-B | 0 | 3 | 3 | 4 | 3 | 3 | 0 |

are denoted as v_{i+} (i=1-6) and v_{i-} (i=1-5), as indicated in the figure. The curve in the figure is symmetric with respect to C_4; the frequencies satisfy the following relations:
\[ v_1^- = v_5^-, \ v_2^- = v_5^+, \ v_3^- = v_4^+, \ v_4^- = v_3^+, \ v_5^- = v_2^+. \]  

**III. Effective Jump Frequency**

In order to derive the expression for the diffusion coefficient by six-jump vacancy cycle, one has to first obtain the effective jump frequency of the cycle in terms of the individual vacancy jump frequencies. The effective jump frequency, \( \bar{v} \), is given by the inverse of the mean expectation time for the vacancy initially in \( C_1 \) to attain \( C_7 \), \( \bar{t} \):

\[ \bar{v} = \frac{1}{\bar{t}}. \]  

The calculation of \( \bar{t} \) begins by writing the rate equations for the probability of occupation, \( P_i \), of various configurations \( C_i \), as follows:

\[
\begin{align*}
\dot{P}_1 &= -4v_1^+ P_1 + 4v_1^- P_2 \quad m_i = 1 \\
\dot{P}_2 &= -(v_1^- + 2v_2^+) P_2 + v_1^+ P_1 + 2v_2^- P_3 \quad 4 \\
\dot{P}_3 &= -(v_2^- + v_3^+) P_3 + v_2^+ P_2 + v_3^- P_4 \quad 4 \times 2 \\
\dot{P}_4 &= -(v_3^- + v_4^+) P_4 + v_3^+ P_3 + v_4^- P_5 \quad 4 \times 2 \\
\dot{P}_5 &= -(v_4^- + v_5^+) P_5 + v_4^+ P_4 + v_5^- P_6 \quad 4 \times 2 \\
\dot{P}_6 &= -(v_5^- + v_6^+) P_6 + v_5^+ P_5 \quad \text{(3)}
\end{align*}
\]

In the above, the multiplicity of each configuration, \( m_i \), are given; \( m_i \) indicates the number of equivalent configurations. It is convenient to define new variables, \( x_i = m_i \times P_i \); \( x_i \) is the probability that any one of the \( i \)-th configuration is realized. The rate equations for \( x_i \) are:

\[
\begin{align*}
\dot{x}_1 &= -4v_1^+ x_1 + v_1^- x_2 \\
\dot{x}_2 &= -(v_1^- + 2v_2^+) x_2 + 4v_1^+ x_1 + v_2^- x_3 \\
\dot{x}_3 &= -(v_2^- + v_3^+) x_3 + 2v_2^+ x_2 + v_3^- x_4 \\
\dot{x}_4 &= -(v_3^- + v_4^+) x_4 + v_3^+ x_3 + v_4^- x_5 \\
\dot{x}_5 &= -(v_4^- + v_5^+) x_5 + v_4^+ x_4 + v_5^- x_6 \\
\dot{x}_6 &= -(v_5^- + v_6^+) x_6 + v_5^+ x_5
\end{align*}
\]

The above equations can be written in matrix form as follows:

\[ \dot{X} = -KX, \quad \text{(5)} \]

where \( X \) is a column vector with elements \( x_1, x_2, \ldots, x_6 \) and \( K \) is the jump frequency matrix:

\[
K = \begin{pmatrix}
4v_1^+ & -v_1^- & 0 & 0 & 0 & 0 \\
-4v_1^+ & (v_1^- + 2v_2^+) & -v_2^- & 0 & 0 & 0 \\
0 & -2v_2^+ & (v_2^- + v_3^+) & 0 & 0 & 0 \\
0 & 0 & -v_3^- & (v_3^- + v_4^+) & -v_4^- & 0 \\
0 & 0 & 0 & -v_4^+ & (v_4^- + v_5^+) & -v_5^- \\
0 & 0 & 0 & 0 & -v_5^+ & (v_5^- + v_6^+)
\end{pmatrix}
\]

For the calculation of the mean expectation time for a vacancy initially in \( C_1 \) to attain \( C_7 \), \( \bar{t} \), the concept of the mean first passage time in the theory of stochastic processes is very useful\(^{(3)}\)(\(^{(6)}\)). We shall briefly explain the method below.

Consider, for example, the decay process of radioactive elements. The concentration of radioactive elements, \( x \), obeys a first-order rate equation:

\[ \dot{x} = -kx. \]  

The mean life time, \( \bar{t} \), is given by the reciprocal of the rate constant \( k \):

\[ \bar{t} = \frac{1}{k}. \]  

In the case of the present problem, the "reaction" occurs by passage through multibarriers and the rate equation can be written in the matrix form as given in eq. (5). By comparing eq. (5) with eq. (7), it seems reasonable to expect that the mean expectation time is related to the reciprocal of the jump frequency matrix. In fact, it can be shown\(^{(6)}\) that the mean expectation time is expressed in terms of the
elements of the inverted matrix of the jump frequency matrix, as
\[ \bar{t} = \sum_{i=1}^{6} \langle i | K^{-1} | 1 \rangle, \]  
(9)
where \( \langle i | K^{-1} | m \rangle \) is the element in the \( i \)-th row and the \( m \)-th column of inverted matrix. For the matrix given eq. (6), the mean expectation time (or the mean life time), \( \bar{t} \), is calculated as
\[ \bar{t} = \left\{ (4v_1 + v_5 + v_6)(3v_2 + v_3 + 2v_5 + v_6 + 2v_3 + v_6) + 4v_1 + v_4 + v_5 + (v_2 + v_3 + v_6 + 2v_3 + v_6 + 2v_5 + v_6) + 8v_1 + v_2 + v_3 + (v_2 + v_3 + v_6 + v_3 + v_6 + 2v_5 + v_6) + 8v_1 + v_2 + v_3 + (v_2 + v_3 + v_6 + 2v_5 + v_6) + 8v_1 + v_2 + v_3 + (v_2 + v_3 + v_6 + 2v_3 + v_6 + 2v_5 + v_6) + 8v_1 + v_2 + v_3 + (v_2 + v_3 + v_6 + 2v_3 + v_6 + 2v_5 + v_6) + 8v_1 + v_2 + v_3 + (v_2 + v_3 + v_6 + 2v_3 + v_6 + 2v_5 + v_6) \right\} / (8v_1 + v_2 + v_3 + v_4 + v_5 + v_6), \]
(10)
where we used the relationships eq. (1).

IV. Diffusion Coefficient

1. Diffusion Coefficient of A atoms, \( D_A \)
The expression for the diffusion coefficient of A atoms can be obtained in a straightforward manner. Once the effective jump frequency, \( \bar{v} \), is defined, the diffusion of A atoms via the six-jump vacancy cycle can now be regarded as the diffusion in the \( \alpha \)-sublattice via simple vacancy mechanism; the diffusion coefficient \( D_A \) is given by
\[ D_A = \frac{1}{4} \bar{v} C_{\alpha\alpha}(\sqrt{2} a)^2 f_A \]
\[ = \frac{1}{2} \bar{v} C_{\alpha\alpha} a^2 f_A, \]  
(11)
where \( C_{\alpha\alpha} \) is the concentration of \( \alpha \)-vacancies and \( f_A \) the correlation factor. The latter is the correlation factor for diffusion via the vacancy mechanism in the square lattice; the quantity has been calculated exactly as(7)
\[ f_A = \frac{1}{\pi - 1} = 0.46694 \cdots. \]  
(12)

2. Diffusion Coefficient of B atoms, \( D_B \)
The calculation of the diffusion coefficient of B atoms, \( D_B \), via the motion of \( \alpha \)-vacancies is not so simple as that of A atoms, \( D_A \), and requires a careful consideration, as described below. In terms of the jump frequency of a B atom to any of neighboring \( \beta \) sublattice sites, \( w_B \), the diffusion coefficient \( D_B \) is written as
\[ D_B = \frac{1}{4} w_B (\sqrt{2} a)^2 f_B = \frac{1}{2} w_B a^2 f_B, \]  
(13)
where \( f_B \) is the correlation factor.

The jump of a B atom (or the exchange of a B atom-pair) occurs when a nearest neighbour \( \alpha \)-vacancy completes the jump cycle (see Fig. 4). Therefore, the jump frequency of a B atom is given by a product of the following two quantities:
- \( 4C_{\alpha\alpha} \): probability of having an \( \alpha \)-vacancy at any of the four corner sites.
- \( (2/4)\bar{v} \): only two out of four possible jumps of the vacancy is effective for the jump of the relevant B atom.
\[ w_B = 4C_{\alpha\alpha} \times \frac{2}{4} \bar{v} = 2C_{\alpha\alpha} \bar{v}. \]  
(14)
Substituting eq. (14) into eq. (13), we obtain
\[ D_B = \bar{v} C_{\alpha\alpha} a^2 f_B. \]  
(15)

Correlation factor of B atom, \( f_B \)
The calculation of the correlation factor, \( f_B \), is an entirely new type of problem. In the six-jump vacancy process, the unit jump of an A atom or the site exchange of an A atom with an \( \alpha \)-vacancy results in the exchange of a B atom pair involved in the jump cycle, and the jump directions of B atoms are perpendicular to that
of $\alpha$-vacancy. Since the vacancy is in the vicinity of the relevant B atom pair just after the exchange, one has to consider the correlation effect. The problem is that of the correlation which originates from the atom movement in the counterpart sublattice. Fortunately, the correlation factor can be calculated rigorously as described below.

The calculation begins by classifying “types” of tracer jumps to be distinguished. Consider the diffusion along the $x$-direction as depicted in Fig. 5; in the square lattice the diffusion is isotropic so that one may choose any convenient direction for the calculation of the diffusion coefficient. The B tracer jumps can be classified into two types, 1 and 2. The tracer jump resulting in the configuration such as shown in Fig. 5(a) is referred to as type 1; the line connecting the tracer and the vacancy is parallel to the $x$-axis. The jump resulting in the perpendicular configuration (Fig. 5(b)) is referred to as type 2. Note that the two types of jumps occur with an equal probability, 1/2. According to Howard\(^8\), the correlation factor component in the $x$ direction may be written in a matrix form as

$$f = 1 + 2b \cdot T(I - T)^{-1} \cdot d,$$

(16)

where $I$ is the $2 \times 2$ unit matrix,

$$b = (c_1 x_1^2 + c_2 x_2^2)^{-1} [c_1 |x_1|, c_2 |x_2|],$$

(17)

c_i is the probability that the type $i$ jump occurs when a tracer jumps, and $x_i$ is the projection of the type $i$ jump in the $x$ direction. In the present problem

$$b = (2a)^{-1} [1, 1],$$

d = a \begin{bmatrix} 1 \\ 1 \end{bmatrix}.$$  

(18)

The elements $t_{\gamma\delta}$ of the matrix, $T$, is

$$t_{\gamma\delta} = p_{\gamma\delta}^+ - p_{\gamma\delta}^-,$$  

(19)

where $p_{\gamma\delta}^+$ are the probabilities that, after an initial tracer jump of type $\gamma$, the next jump is of type $\delta$ and has the same (+) or opposite (−) $x$-component.

The elements $t_{\gamma\delta}$ are calculated as explained below. Consider the case that a tracer B atom has just made a type 1 jump with a positive $x$ component. Figure 6 shows the resulting configuration. For convenience’s sake the $\alpha$-sublattice sites are indicated by the coordinates $(u, v)$ and the $\beta$-sublattice sites are named as K, L, M, N and O, as shown in Fig. 6(a). The tracer has jumped from L and now at O with the vacancy jump from $(1, 0)$ to $(0, 0)$; the tracer jump L→O is type 1 and has the positive $x$ component.

For the tracer at O to make a next jump, the vacancy must be at any of the four neighbouring sites and make any of the eight jumps indicated by arrows in Fig. 6(a). Table 2 lists vacancy jumps, associated tracer jumps, type of jumps and the sign of the $x$ displacement of the tracer. With the help of the table, the probability, $p_{\gamma\delta}^+$, that after an initial tracer jump of type 1, the next jump is of type 1 and has the same $x$-component, can be written as

$$p_{11}^+ = \frac{1}{4} (2W(1, 1)) = \frac{1}{2} W(1, 1),$$

(20)

where $W(u, v)$ is the probability of finding the
vacancy at the \((u, v)\) site. The factor 1/4 comes from the fact that the vacancy can jump into any of the four directions with an equal probability; one-fourth of the vacancy jumps is effective to induce a particular tracer jump. Similarly, the probability \(p_{11}\) is

\[
p_{11} = \frac{1}{4} (2W(0, 0)) = \frac{1}{2} W(0, 0).
\]  

(21)

By substituting eqs. (20) and (21) into (19), \(t_{11}\) is expressed as

\[
t_{11} = \frac{1}{2} (W(1, 1) - W(0, 0)).
\]  

(22)

In reference to Table 2, \(t_{12}\) is calculated as

\[
t_{12} = \frac{1}{4} \{W(0, 1) + W(1, 0) - (W(0, 1) + W(1, 0))\} = 0.
\]  

(23)

For an initial type 2 jump, one eventually shows that

\[
t_{22} = 0, \ t_{21} = 0
\]  

(24)

by adopting a similar procedure to that for \(t_{11}\). More directly, this result is almost self-evident from the relative configuration of vacancy and tracer; positive and negative tracer jumps are equally probable for the perpendicular configuration.

The calculation of the number of visits, \(W(u, v)\), should be made by dropping out the contribution of the vacancy jumps indicated by the arrows in the figure; such jumps would result in the movement of the tracer B atom at

Table 2 Classification of tracer jumps after a type 1 (positive) jump.

| Vacancy position before jump | Tracer position after jump | Type | Sign of \(x\) displacement |
|-----------------------------|---------------------------|------|--------------------------|
| \((0, 0)\)                  | \((0, 1)\)                | K    | 1                        |
| \((1, 0)\)                  | \((0, 0)\)                | L    | 1                        |
| \((0, 1)\)                  | \((1, 1)\)                | N    | 2                        |
| \((1, 0)\)                  | \((0, 0)\)                | L    | 2                        |
| \((1, 1)\)                  | \((1, 0)\)                | M    | 2                        |
| \((0, 1)\)                  | \((1, 0)\)                | N    | 1                        |
| \((1, 1)\)                  | \((1, 1)\)                | M    | 1                        |

Fig. 6 Relationship between a vacancy jump and a B atom jump (see text). The configurations of vacancy and B atom are (a) parallel and (b) perpendicular to the \(x\) direction.
the center of the square. At first sight this limitation seems to make the calculation very complicated.

Note that, however, we are only interested in the combined quantity, \( W(1, 1) - W(0, 0) \), but not individual quantities. It is evident from the figure that the vacancy arrived at the sites on the symmetry axis \( ss' \) has an equal contribution to both \( W(1, 1) \) and \( W(0, 0) \); the difference of the two quantities is not affected by the restriction. Therefore, the number of visits may be calculated for a random walk sequence starting from origin without any restriction; from the theory of “unrestricted” random walks the number of visits is expressed in terms of the lattice Green functions, \( G(u, v) \):

\[
W(1, 1) - W(0, 0) = G(1, 1) - G(0, 0). \quad (25)
\]

Actually, for a two-dimensional random walk, \( G(u, v) \) is infinite. But the difference such as that appearing in eq. (25) has a finite value as described by McCrea and Whipple(9). In reference to the tabulated result of their paper, \( t_{11} \) is

\[
t_{11} = \frac{1}{2} (G(1, 1) - G(0, 0)) = -\frac{2}{\pi}. \quad (26)
\]

Substitution of \( t_{11} \) into eq. (16) yields the correlation factor \( f_0 \) as

\[
f_0 = \frac{\pi}{\pi + 2} = 0.61101 \ldots . \quad (27)
\]

V. Discussion

1. The ratio of diffusion coefficients

In the preceding section we consider the case of \( \alpha \) vacancies. In this section we discuss the case that vacancies exist in both \( \alpha \) and \( \beta \) sublattices. It is assumed that the concentration of vacancies in each sublattice is not so large that the motion of vacancies does not interfere each other. Then the diffusion coefficients of \( A \) and \( B \) atoms is given by

\[
D_A = \frac{1}{2} \bar{v}^\alpha C_{V\alpha} \delta^2 f_A + \bar{v}^\beta C_{V\beta} \delta^2 f_B
\]

\[
D_B = \frac{1}{2} \bar{v}^\beta C_{V\beta} \delta^2 f_A + \bar{v}^\alpha C_{V\alpha} \delta^2 f_B \quad (28)
\]

where the subscripts \( \alpha \) and \( \beta \) indicate that the relevant quantities are related to the respective sublattice. The ratio of the two diffusion coefficients, \( D_A / D_B \), in the binary alloys has attracted much attention in previous theoretical and experimental investigations. From eq. (28), the ratio is

\[
R = \frac{D_A}{D_B} = \frac{\bar{v}^\alpha C_{V\alpha} f_A + 2 \bar{v}^\beta C_{V\beta} f_B}{\bar{v}^\beta C_{V\beta} f_A + 2 \bar{v}^\alpha C_{V\alpha} f_B}
\]

\[
= \frac{f_A + 2 f_\alpha r}{f_\beta r + 2 f_B} \quad (29)
\]

where

\[
r = \frac{\bar{v}^\beta C_{V\beta}}{\bar{v}^\alpha C_{V\alpha}}. \quad (30)
\]

Since \( r \) may take any positive values, \( 0 < r < \infty \), one obtains the following inequality:

\[
\frac{f_A}{2 f_B} < R < \frac{2 f_B}{f_A}, \quad (31)
\]

or

\[
\frac{\pi + 2}{2 \pi (\pi - 1)} = 0.38210 \ldots < R < 2.6170 \ldots . \quad (32)
\]

In the argument of previous investigators (see, e.g. Ref. 10), the existence of correlation effect has been ignored, which is equivalent to assume \( f_A = f_B = 1 \); the corresponding relation derived by other investigators is

\[
\frac{1}{2} < R < 2. \quad (33)
\]

2. Temperature dependence of the effective jump frequency

The expression for the diffusion coefficients, such as eq. (28), contains two quantities which depend on temperature. \( C_V \) is known to have simple dependence on temperature: \( C_V \propto \exp (-E_f / kT) \), where \( E_f \) is the formation energy of vacancy. In contrast, the effective jump frequency, \( \bar{v} \) is a complicated function of \( v_{1+}, v_{2+}, \ldots, \) and \( v_{6+} \), and requires a detailed examination of its temperature dependence. For such analyses, it is necessary to specify numerical values for individual vacancy frequencies. We shall consider the following case:
$v_i = v_0 \exp \left( -\frac{E_0}{kT} \right)$ for $i = 1, 2, 3$
$v_1 = v_0 \exp \left( -\frac{E_0 + 3E_{BB}}{kT} \right) = v\alpha^3$
$v_2 = v_0 \exp \left( -\frac{E_0 + 2E_{AA}}{kT} \right) = v\beta^2$
$v_3 = v_0 \exp \left( -\frac{E_0 + E_{BB}}{kT} \right) = v\alpha^2$
$\alpha = \exp \left( -\frac{E_{AA}}{kT} \right)$
$\beta = \exp \left( -\frac{E_{BB}}{kT} \right)$

where $E_{AA}$ and $E_{BB}$ are the wrong bond energy of A-A and B-B atom pairs, respectively. The effective jump frequency, $\bar{v}$, can be expressed in terms of $\alpha$ and $\beta$ as follows. Substituting eq. (34) into eq. (10), we obtain

$$\bar{v} = 8\alpha^2\beta^4 / (16\alpha^4\beta^5 + 16\alpha^4\beta^4 + 8\alpha^2\beta^3 + 3\alpha^2\beta^4 + 16\alpha^2\beta^3 + 8\beta^4 + 8\beta^3 + 3\alpha^2\beta^2 + 2\alpha^2 + 2\beta^2)$$

(35)

For several sets of values for $v_0$, $E_0$, $E_{AA}$, and $E_{BB}$ the temperature dependence of $\bar{v}$ has been calculated. The solid line in Fig. 7 is drawn for a set of values: $v_0=10^{13} \text{ s}^{-1}$, $E_0=3.0 \text{ eV}$, $E_{AA}=E_{BB}=0.05 \text{ eV}$. The plot is substantially straight for a wide range of temperature. With decreasing temperature, $\alpha$ and $\beta$ tends to zero, so that $\bar{v}$ asymptotically approaches the following equation:

$$\bar{v} = 4\alpha^2\beta^4 = 4 \times 10^{13} \exp \left( -\frac{E'}{kT} \right)$$

(36)

where

$$E' = E_0 + 4E_{BB} + 2E_{AA}.$$
3. Other jump paths

In the above, we have considered the six-jump cycle, because the maximum number of wrong bonds formed during cycle is the smallest for such a path. If we allow the formation of a larger number of wrong bonds, there are a number of other possible paths. Figure 8 illustrates some of such jump cycles: ten- and fourteen-jump cycles, together with the six-jump cycle.

In order to assess the relative importance of various cycles, the number of wrong bonds is plotted as a function of jump steps of vacancy in Fig. 9. The general trend is that with the increase in the number of vacancy jumps required for the completion of the cycle, the maximum number of wrong bonds, and so the energy of system increase. Therefore, the occurrence of various jump cycles is considered to be less frequent than that of the six-jump cycle. A quantitative estimation of the relative importance of various cycles can be made, in principle, if the wrong bond energy is given.

VI. Conclusions and Summary

As a first step for understanding the diffusion process in ordered alloys or intermetallic compounds, the atom movements in a two-dimensional square lattice are analysed in detail on the basis of six-jump vacancy cycle model. The effective jump frequency, $\bar{v}$, for the cycle is calculated from the rate equations for the probability of various configurations during the cycle; $\bar{v}$ is given in terms of individual vacancy jump frequencies.

The other important quantities appearing in the expression for the diffusion coefficients are correlation factors; two correlation factors $f_A$ and $f_B$ are required in the present problem. The correlation factor, $f_A$, is nothing but the correlation factor for diffusion via the vacancy mechanism in the square lattice. The exact value was previously calculated by Montet\(^7\) as

$$f_A = 0.46694 \cdots .$$

The other correlation factor, $f_B$, is newly calculated as

$$f_B = 0.61101 \cdots .$$

The ratio of the two diffusion coefficients via the six-jump vacancy cycle should satisfy the following inequality:

$$0.38210 \cdots < D_A / D_B < 2.6170 \cdots ,$$

This should be compared with the inequality which has been accepted by previous investigators;

$$1/2 < D_A / D_B < 2.$$

The analysis of the diffusion process in three-dimensional ordered alloys are in progress, and will be reported soon.

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