Correlation Factors for Impurity Diffusion—fcc Lattice

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The correlation factor f for an isolated impurity atom diffusing by a vacancy mechanism in a face-centered cubic lattice is calculated in terms of five vacancy jump frequencies near the impurity, w_0, w_1, w_2, k_1, and k_2, as defined by Lidiard. In general, the correlation factor can be expressed as $f=(2w_1+7Fk_1)/(2w_2+2w_1+7Fk_1)$, where F is a function of k_2/w_0. In the limit where $k_2/w_0\rightarrow 0$, F goes to unity. In the limit where $k_2/w_0\rightarrow\infty$, F goes to 2/7. When the five frequencies above are the only vacancy jump frequencies in the crystal, an expression for F as a function of k_2/w_0 can be found from a Bardeen-Herring calculation. It is found that

$$F=1-\frac{S}{7}\left(\frac{11.56+50.10\Delta+40.00\Delta^2}{0.521+4.71\Delta+12.06\Delta^2+8.00\Delta^3}\right),$$

where $S=k_2/12w_0$ and $\Delta=(k_2-w_0)/12w_0$. This method can be extended to other lattices. Applications to data in the literature are discussed.

I. INTRODUCTION

IT is generally agreed that diffusion in crystals takes place by each atom making a series of jumps from one site to another throughout the crystal. If each atom pursues a random walk, the diffusion coefficient D for isotropic diffusion is given by

$$D=\tfrac{1}{6}\lambda^2\nu, \tag{1}$$

where λ is the jump distance and ν the jump frequency. However, if the direction of a diffusive jump depends to some extent on the direction of a previous jump, the usual random walk treatment must be modified. Then,[1–3]

$$D=\tfrac{1}{6}\lambda^2\nu f, \tag{2}$$

where the additional factor f (called the correlation factor) takes into account the correlation between the directions of successive atom jumps.

In the present paper, a general expression for the correlation factor for an impurity diffusing by a vacancy mechanism in a face-centered cubic lattice is derived in terms of five vacancy jump frequencies. Attention is centered on the face-centered cubic lattice; however, the general method used here can be applied to other cubic lattices also.

2. IMPURITY DIFFUSION IN A FACE-CENTERED CUBIC LATTICE

Following Lidiard's notation,[4] one may designate vacancy jump frequencies in a face-centered cubic lattice as follows: (1) w_2 is the frequency for exchange with a neighboring impurity atom, (2) w_1 is the frequency for exchange with a neighboring solvent atom when the vacancy and solvent atom are both nearest neighbors of the same impurity, (3) k_1 is the frequency when the vacancy is a nearest neighbor of an impurity but the solvent atom is not, (4) k_2 is the frequency when the solvent atom is a nearest neighbor of an impurity, but the vacancy is not, and (5) w_0 is the frequency when neither the vacancy nor the solvent is a nearest neighbor of an impurity. It may be noted that the k_2 jumps are just the reverse of the k_1 jumps. Since the k_2 jumps cause a vacancy to become a nearest neighbor of an impurity, they are called *associative* jumps. Since the k_1 jumps move a vacancy away from an impurity, they are called *dissociative* jumps.

In a previous paper,[5] it was shown that the correlation factor for diffusion of an impurity by a vacancy mechanism in a face-centered cubic lattice is given by

$$f=\frac{2w_1+7Fk_1}{2w_2+2w_1+7Fk_1}, \tag{3}$$

where F is the fraction of dissociating vacancies (those making k_1 jumps) which effectively do not return to the site from which the k_1 jump was made. The probability of return depends on the relative values of the vacancy jump frequencies when the vacancy is not a nearest neighbor of the impurity. If k_2 and w_0 are the only two such frequencies, F depends only on geometric factors and the ratio k_2/w_0.

The value of F can be calculated quite easily in a few special cases. For example, if k_2 equals zero, no vacancies return after dissociating, and F equals unity. Thus, if $k_2/w_0\rightarrow 0$, Eq. (3) reduces to

$$f=\frac{2w_1+7k_1}{2w_2+2w_1+7k_1}, \tag{4}$$

as was determined previously by Lidiard and LeClaire.[2,4]

Equation (3) must also be valid for self-diffusion, where $w_2=w_1=k_1=k_2=w_0$. Compaan and Haven[3,6] find

[1] J. Bardeen and C. Herring, in *Atom Movements* (American Society for Metals, Cleveland, 1951), p. 87; also in *Imperfections in Nearly Perfect Crystals*, edited by W. Shockley (John Wiley & Sons, Inc., New York, 1952), p. 261.
[2] A. D. LeClaire and A. B. Lidiard, Phil. Mag. **1**, 518 (1956).
[3] K. Compaan and Y. Haven, Trans. Faraday Soc. **52**, 786 (1956).
[4] A. B. Lidiard, Phil. Mag. **46**, 1218 (1955).
[5] J. R. Manning, Phys. Rev. **116**, 819 (1959).
[6] K. Compaan and Y. Haven, Trans. Faraday Soc. **54**, 1498 (1958).

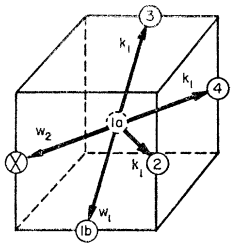

FIG. 1. Face-centered cubic lattice. Sites designated 1, 2, 3, and 4, are first, second, third, and fourth nearest neighbors of the impurity ×. The arrows with w_1, w_2, and k_1 denote the vacancy jump frequencies. A k_2 jump is merely the reverse of a k_1 jump.

that the correlation factor for self-diffusion in the face-centered cubic lattice equals 0.78146. When these values are substituted into Eq. (3), one finds F must equal 0.7359. Since F does not depend on w_2, w_1, or k_1, F will have this value whenever k_2 equals w_0. Thus, whenever $k_2=w_0$, Eq. (3) reduces to

$$f=\frac{2w_1+5.151k_1}{2w_2+2w_1+5.151k_1}. \tag{5}$$

A third special case which might be treated is that where $k_2/w_0\rightarrow\infty$. At first glance, one might expect F to equal zero in this case, since all dissociating vacancies must return to the impurity. However, as will be seen later, F equals 2/7 when $k_2/w_0\rightarrow\infty$, and the coefficient of k_1 in Eq. (3) equals 2.

After these special cases have been considered, the next step is to obtain a general expression giving F as a function of k_2/w_0. This is done in the present paper. To accomplish this, vacancy jumps from both the first and second coordination shells around the impurity are treated in detail. The first coordination shell includes all sites that can be reached in one jump from the site occupied by the impurity. The second coordination shell includes all sites that can be reached in two jumps away from the impurity. In a face-centered cubic lattice, the first coordination shell contains just the nearest neighbors of the impurity; however, the second coordination shell contains second, third, and fourth nearest neighbors. (See Fig. 1.)

3. DERIVATION OF AN EXPRESSION FOR F

A. Symmetric Sites

In calculating the impurity correlation factor (and F), one may consider an impurity atom that has just made a diffusive jump by exchanging places with a vacancy. In a cubic crystal, the correlation factor can be calculated directly from the average cosine of the angle between the direction of this jump and that of the next jump taken by the impurity.[2,3] This calculation can be aided by consideration of the crystal symmetry.

Without loss of generality, one may orient the crystal so that the vacancy which has just exchanged with the impurity is on site a, the site to the right of the impurity. Also, the general angle θ_ρ may be defined as the angle between the line connecting the vacancy to the impurity and the line connecting the impurity to the various sites ρ in the crystal. Then, the crystal sites can be divided into groups[2] so that θ_ρ and the distance of the various sites from the impurity are the same for all sites in a given group. There are five such groups for sites in the first coordination shell in the face-centered cubic lattice. These groups can be designated as groups a to e. (See Fig. 2.) There are fifteen such groups in the second coordination shell. These groups can be designated as groups g to u. (See Fig. 3.) Values of $\cos\theta_\rho$ and the nearest-neighbor classifications for these groups are listed in Table I.

TABLE I. Conversion factors for equivalent distributions.

Group	Nearest-neighbor classification[a]	$\cos\theta_\rho$	Equivalent distributions[b] on sites a, g, h, and i
a	1	-1	a
b	1	$-1/2$	$\frac{1}{2}a$
c	1	0	0
d	1	$+1/2$	$-\frac{1}{2}a$
e	1	$+1$	$-a$
g	4	-1	g
h	3	$-3/2\sqrt{3}$	h
i	2	$-1/\sqrt{2}$	i
j	3	$-2/2\sqrt{3}$	$\frac{2}{3}h$
k	4	$-1/2$	$\frac{1}{2}g$
l	3	$-1/2\sqrt{3}$	$\frac{1}{3}h$
m	2	0	0
n	3	0	0
o	4	0	0
p	3	$+1/2\sqrt{3}$	$-\frac{1}{3}h$
q	4	$+1/2$	$-\frac{1}{2}g$
r	3	$+2/2\sqrt{3}$	$-\frac{2}{3}h$
s	2	$+1/\sqrt{2}$	$-i$
t	3	$+3/2\sqrt{3}$	$-h$
u	4	$+1$	$-g$

[a] First nearest neighbors are designated by 1, second nearest neighbors by 2, third nearest neighbors by 3, and fourth nearest neighbors by 4.
[b] For example, a distribution with two vacancies on sites b will be equivalent to a distribution with one vacancy on site a, since $2b=2(\frac{1}{2}a)=a$.

B. Equivalent Distributions

A vacancy which has made a dissociative jump from site a may subsequently make an associative jump, which returns it to a site on the first coordination shell. In all cubic lattices, there is either two- or threefold rotational symmetry around the line connecting the

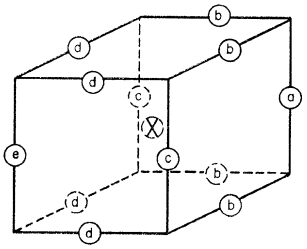

FIG. 2. Face-centered cubic lattice. Nearest neighbors of the impurity × are designated by a, b, c, d, or e according to their positions relative to sites × and a.

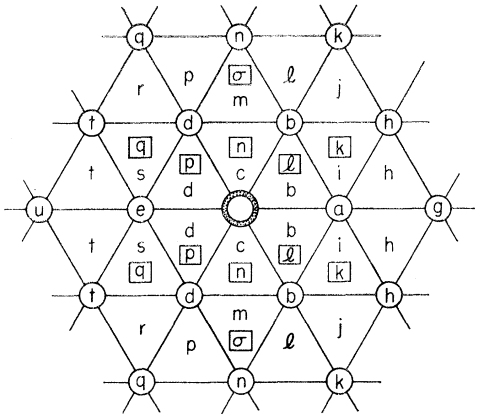

FIG. 3. Lattice sites in the first and second coordination shells in a face-centered cubic lattice. The sites are projected on the (111) plane containing the impurity and site a. The impurity is the large atom in the center of the drawing. Sites in the first coordination shell are indicated by the letters a to e. Sites in the second coordination shell are indicated by the letters g to u. Sites indicated by circles and connected by straight lines lie in the same (111) plane as the impurity and site a. Those standing free inside the large triangles lie on the (111) planes immediately above or below the plane of the drawing. Those inside the rectangles lie on the second planes above and below the plane of the drawing. In an accurate projection, all sites indicated inside the large triangles would project directly at the center of these triangles.

impurity to a neighboring site. Because of this symmetry, the probability of a vacancy returning to one site in a given group a to e is the same as the probability of it returning to any other particular site in that group. Also, the actual probabilities of return to the various nearest neighbor sites have an effect on the average cosine (and hence on the correlation factor) equivalent to a certain probability of return to site a alone.[5] Thus, for our purposes, a vacancy distribution on the various nearest-neighbor sites can be replaced by an equivalent distribution on site a; and a certain fraction of the vacancies which actually return to sites b, c, d, and e can be thought of as having "effectively" returned to site a.

The same principle of equivalent distributions can be applied to second, third, and fourth nearest neighbors. A vacancy distribution on the second nearest-neighbor sites may be replaced by an equivalent distribution on sites i, a vacancy distribution on the third nearest-neighbor sites by an equivalent distribution on sites h, and a vacancy distribution on the fourth nearest-neighbor sites by an equivalent distribution on site g. If P_α is the probability of a vacancy being at site α, the equivalent probability P_γ at site γ is given by

$$P_\gamma \cos\theta_\gamma = P_\alpha \cos\theta_\alpha. \tag{6}$$

The equivalent distributions on sites a, g, h, and i are listed in Table I. The numerical coefficients in the last column of Table I, equal to P_γ/P_a, were determined from Eq. (6) and the cosine values which are listed in the third column of Table I. Use of these equivalent distributions greatly simplifies the calculation of F.

C. Calculation of F when $k_2/w_0 \to \infty$

In the calculation of the correlation factor, vacancies which effectively return to site a can be treated as if they had never left site a at all. Thus, the actual frequency $7k_1$ of dissociative jumps from site a can be replaced by an effective frequency $7Fk_1$, as in Eq. (3). By definition, F is the fraction of dissociating vacancies which do *not* effectively return to site a. One finds by summing over all possible k_1 jumps from site a,

$$1-F = P_g(k_1)G_R + P_h(k_1)H_R + P_i(k_1)I_R, \tag{7}$$

where $P_g(k_1)$, $P_h(k_1)$, $P_i(k_1)$ are the probabilities that the k_1 jump will take the vacancy to a site g, h, or i; and G_R, H_R, I_R are the probabilities that the vacancy will effectively return to site a from a site g, h, or i.

As a simple example, one may consider the case where all k_1 jumps are equally likely and $k_2/w_0 \to \infty$. There are four h sites, two i sites, and one g site. Thus, $P_g(k_1)=1/7$, $P_h(k_1)=4/7$, and $P_i(k_1)=2/7$. When $k_2/w_0 \to \infty$, the next jump of the vacancy after a k_1 jump must be a k_2 jump, which will return it to the first coordination shell. From site g, the vacancy can return only to site a. Thus, all vacancies from site g actually return to site a, and $G_R=1$ in this case. From a site h, the vacancy may jump either to site a or to a site b. As a result, one finds $H_R=\frac{1}{2}(1+\frac{1}{2})$. The factor $\frac{1}{2}$ in front of the parentheses arises because there are two equally likely k_2 jumps for a vacancy from site h, whose contributions must be averaged. The factor $(1+\frac{1}{2})$ gives the effective probability of return contributed from each of these jumps. Here vacancies which return directly to site a give a unit contribution, but those which return to a site b give only a half-unit contribution. (According to Table I, a vacancy at a site b is equivalent to half a vacancy at site a). From a site i, the vacancy can jump to site a, to two b sites, or to a site c. According to Table I, a vacancy on a site c leads to zero equivalent distribution on site a. Thus, by the same reasoning as that above, $I_R=\frac{1}{4}(1+\frac{1}{2}+\frac{1}{2}+0)$. When these values are substituted in Eq. (7), one finds

$$1-F=\left(\frac{1}{7}\right)(1)+\left(\frac{4}{7}\right)\left(\frac{3}{4}\right)+\left(\frac{2}{7}\right)\left(\frac{1}{2}\right), \tag{8}$$

and

$$F=2/7. \tag{9}$$

It may be noted that F does not go to zero even when $k_2/w_0 \to \infty$. The k_2 jump from a site h or i does not need to be the reverse of the preceding k_1 jump. This allows H_R and I_R to be smaller than unity and leads to a value of F greater than zero. Similar results are found in most other cubic lattices. Physically, F is the fraction of k_1 jumps which result in the vacancy effectively escaping from site a. Those vacancies which return on the next jump directly to site a have not effectively escaped from this site and can be treated as if they had never left site a at all. However, vacancies which arrive at a

site b or c after a k_2 jump from a site h or i have partially escaped from site a. This makes F larger than zero. The partial escape of the vacancy from site a allows the impurity greater freedom in its direction of jump. Thus, it also increases the correlation factor.

D. General Expressions for G_R, H_R, and I_R

A vacancy, immediately after making a k_1 jump from site a, will find itself on the second coordination shell on a site g, h, or i. If it returns to the first coordination shell on its next subsequent jump, it can be considered, at least partially, to have returned to site a, as discussed above. When $k_2/w_0 \neq \infty$, the vacancy very likely will *not* return to the first coordination shell on this next jump. It may, however, either on this jump or some subsequent jump, arrive at a site on the second coordination shell. From here, it then can return to the first coordination shell. This probability of indirect return in two or more vacancy jumps must be included if one wishes to calculate the full probability of effective return for arbitrary k_2/w_0. First, the distributions of vacancies which arrive at the various sites on the second coordination shell can be calculated. Then one can find the probability that these vacancies will return to the first coordination shell and contribute to F. From this, a general expression for F in terms of k_2/w_0 can be obtained. This is discussed in the following paragraphs.

As was noted above, a vacancy distribution on the second coordination shell can be replaced by an equivalent distribution on sites g, h, and i. One can define G_g, G_h, and G_i as the equivalent distributions on sites g, h, and i, respectively, arising from vacancies which start on site g and return to all the various sites g to u on the second coordination shell. Similarly, one can define H_g, H_h, and H_i as the equivalent distributions for vacancies which start on a site h, and I_g, I_h, and I_i as those for vacancies which start on a site i. Only the first site on the second coordination shell which the vacancy reaches after leaving its starting point (g, h, or i) should be included in determining the effective arrival probabilities G_g, H_g, I_g, etc.

One can use these quantities to obtain general expressions for G_R, H_R, and I_R. For example,

$$G_R = G_a + G_g G_R + 4G_h H_R + 2G_i I_R. \tag{10}$$

Here G_a represents the effective probability of return from jumps that take the vacancy directly from site g to a site neighboring on the impurity. This is the term considered in Sec. C. The other three terms on the right represent the contributions from paths which require two or more jumps to return the vacancy to a nearest-neighbor site. For example, the term $2G_i I_R$ contains the effective probability G_i that the vacancy will arrive at one of the i sites after one or more jumps from site g multiplied by the probability I_R that it will then effectively return to site a. The factor 2 arises because there are two i sites. Similarly, the term $4G_R H_R$ gives the effective probability that the vacancy will arrive at an h site and then subsequently return to site a. (There are four h sites.) Also, $G_g G_R$ gives the effective probability that the vacancy will arrive back at site g and then return to a. By following this same pattern, one obtains equations for H_R and I_R,

$$H_R = H_a + H_g G_R + 4H_h H_R + 2H_i I_R, \tag{11}$$

$$I_R = I_a + I_g G_R + 4I_h H_R + 2I_i I_R. \tag{12}$$

E. Calculation of Coefficients

Equations (10)–(12) give recursion relations between G_R, H_R, and I_R. It is only necessary to calculate the coefficients G_a, H_a, I_a, G_g, H_g, I_g, etc., in order to obtain numerical values for G_R, H_R, and I_R. These values then can be substituted into Eq. (7) to give an explicit expression for F.

The method of determining G_a, H_a, and I_a has already been discussed in Sec. C. The expressions in Sec. C must be modified, however, to take into account the increased number of possible jumps from sites g, h, and i. This may be done by adding a factor giving the probability that a jump from a site g, h, or i will be a k_2 jump. In general, $G_a = (1)[k_2/(11w_0+k_2)]$; $H_a = (\frac{3}{4})[2k_2/(10w_0+2k_2)]$; and $I_a = (\frac{1}{2})[4k_2/(8w_0+4k_2)]$. The denominators in these expressions equal the total jump frequency from sites g, h, and i, and the numerators equal the effective frequency of return to site a by a k_2 jump.

The quantities G_g, H_g, I_g, etc., can be determined by a straightforward Bardeen-Herring diffusion of probability calculation.[1] One first calculates the probability that the vacancy will arrive at the various sites on the second coordination shell after one jump from the original site (g, h, or i). Then those vacancies which have arrived at sites on the first or second coordination shells are removed from further consideration, and one proceeds to calculate the probability that the remaining vacancies will arrive at a site on the second coordination shell on the next jump. This can be repeated for as many jumps as necessary. The total probability of a vacancy arriving at a given site is found by summing the probability of the vacancy arriving at this site after each of the various jumps. The equivalent distributions on sites g, h, and i can then be calculated from the values of $\cos\theta$ given in Table I. Summing all contributions from sites which are fourth nearest neighbors of the impurity gives G_g, H_g, and I_g; summing all contributions from third nearest neighbors gives G_h, H_h, and I_h; and summing all contributions from second nearest neighbors gives G_i, H_i, and I_i.

The effective return probabilities for a face-centered cubic lattice were calculated by the above method. In each case, the vacancy distribution was calculated in detail for six jumps, and the probability that a vacancy would arrive at a site in the second coordination shell was determined for these jumps (jumps number one to

TABLE II. Effective arrival probabilities and effective probabilities of direct return.

$G_g=1.25\,w_0/(11w_0+k_2)$	$H_g=2.20\,w_0/(10w_0+2k_2)$	$I_g=0.42\,w_0/(8w_0+4k_2)$
$G_h=1.42\,w_0/(11w_0+k_2)$	$H_h=0.77\,w_0/(10w_0+2k_2)$	$I_h=0.89\,w_0/(8w_0+4k_2)$
$G_i=0.160\,w_0/(11w_0+k_2)$	$H_i=0.68\,w_0/(10w_0+2k_2)$	$I_i=0.245\,w_0/(8w_0+4k_2)$
$G_a=k_2/(11w_0+k_2)$	$H_a=\frac{2}{3}k_2/(10w_0+2k_2)$	$I_a=2\,k_2/(8w_0+4k_2)$

six). Then, the contributions from the remaining jumps (jumps number seven to infinity) were estimated by assuming that successive contributions would continue to decrease in a regular manner. The contribution from these remaining jumps will be small (less than 10% of the total) and the trend in the contribution from each successive jump seems well established by the detailed calculations for the first six jumps. Thus, the error in these estimations should be small. This should introduce very little error in the final figures for G_g, H_g, I_g, etc. The final values are given in Table II. It is believed that in most cases the error is less than 2% of these values. The accuracy in the final expression for F seems to be even better than this.

F. Equation for F

When values of the G, H, and I quantities from Table II are substituted into Eqs. (10)–(12) one obtains

$$(0.896+\Delta)G_R-0.473H_R-0.0267I_R=S, \quad (13)$$

$$-0.183G_R+(0.743+2\Delta)H_R-0.113I_R=1.5S, \quad (14)$$

$$-0.035G_R-0.297H_R+(0.959+4\Delta)I_R=2S, \quad (15)$$

where

$$\Delta=(k_2-w_0)/12w_0, \quad (16)$$

and

$$S=k_2/12w_0. \quad (17)$$

Equations (13)–(15) can be solved for G_R, H_R, and I_R. When this is done, one finds

$$G_R=\sigma^{-1}S(1.52+7.84\Delta+8.00\Delta^2), \quad (18)$$

$$H_R=\sigma^{-1}S(1.68+7.77\Delta+6.00\Delta^2), \quad (19)$$

$$I_R=\sigma^{-1}S(1.66+5.59\Delta+4.00\Delta^2), \quad (20)$$

where

$$\sigma=0.521+4.71\Delta+12.06\Delta^2+8.00\Delta^3. \quad (21)$$

When these values are substituted into Eq. (7), with all k_1 jumps assumed equally likely, one obtains

$$F=1-\frac{S}{7}\left(\frac{11.56+50.10\Delta+40.00\Delta^2}{0.521+4.71\Delta+12.06\Delta^2+8.00\Delta^3}\right). \quad (22)$$

4. DISCUSSION

The value of F as given by Eq. (22) depends only on the ratio k_2/w_0. Figure 4 shows $7F$, which is the coefficient of k_1 in Eq. (3), as a function of k_2/w_0. This varies from seven for $k_2/w_0\to 0$ to two for $k_2/w_0\to\infty$. In no case does the coefficient of k_1 equal zero. If $k_2=w_0$, the quantity Δ equals zero, and S equals (1/12). Thus Eq. (22), in agreement with Eq. (4), yields $7F=5.15$ when $k_2=w_0$.

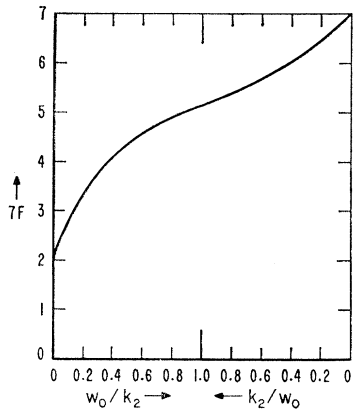

FIG. 4. Plot of $7F$ as a function of w_0/k_2 (from left to center) and k_2/w_0 (from right to center).

In the derivation of Eq. (22), it was assumed that k_1 and k_2 do not depend on the type of site (g, h, or i) in the second coordination shell which is involved in the vacancy jump. One can, without great effort, refine this model and assume separate jump frequencies for each of these sites. (Extensive additional calculations are necessary only if frequencies different from w_0 are assigned to jumps outside the first coordination shell.) However, the introduction of other jump frequencies, whose value is not known, complicates the final expression and does not lead to any new understanding of experimental results. Thus, it seems that a better approach is to regard k_1 and k_2 as average values, averaged over the sites g, h, and i.

The presence of an impurity may affect solvent-vacancy jump frequencies at considerable distances from the impurity. This would result in there being many more jump frequencies than the five considered here. However, the main jump frequencies affecting F are those for a vacancy in the second coordination shell. Thus, for any reasonable group of jump frequencies varying monotonically with distance from the impurity, a good approximation to F can be obtained merely by replacing w_0 in Eq. (22) with an average frequency, averaged over all jumps from sites on the second coordination shell to sites on the second or third coordination shell.

5. COMPARISON WITH EXPERIMENT

A. Correlation Factor

When impurity correlation factors can be measured experimentally, Eq. (22) can help determine jump frequency ratios. For example, Mullen has shown[7]

$$f_i=1-\frac{f_s(D_i/D_s)(w_0/k_2)}{(w_1/k_1)+3.5F}, \quad (23)$$

[7] J. G. Mullen, Phys. Rev. **121**, 1649 (1961).

where f_i and f_s are the impurity and solvent correlation factors and D_i and D_s are the impurity and solvent diffusion coefficients. This equation can give limiting values for k_2/w_0.

At present, isotope effect experiments seem to provide the best means of measuring impurity correlation factors. Two isotopes of the same impurity will have slightly different jump frequencies because of their difference in mass. It has been shown[8,9] that the measured difference in diffusion coefficient ΔD will be related to the difference in jump frequencies Δw by the equation

$$\Delta D/D_\beta = f_\alpha(\Delta w/w_\beta), \tag{24}$$

where f_α is the correlation factor of one of the isotopes and D_β and w_β are the diffusion coefficient and jump frequency of the other. According to classical rate theory,[10,11] the jump frequency should be inversely proportional to the square root of the mass. Thus, according to this theory,

$$\Delta w/w_\beta = (m_\beta/m_\alpha)^{1/2} - 1, \tag{25}$$

where m_α and m_β are the masses of the two isotopes; and the experimental quantity E, where

$$E = \frac{(\Delta D/D_\beta)}{(m_\beta/m_\alpha)^{1/2} - 1}, \tag{26}$$

will equal f_α.

Mullen[7] has measured values of E for Fe^{55} and Fe^{59} diffusing in copper and silver. He finds values of E as low as 0.59 for diffusion in copper and 0.49 for diffusion in silver. If it is assumed that Eq. (25) is very nearly correct and hence that $E \approx f_\alpha$, one can use Mullen's values of E along with Eqs. (22)–(23) and appropriate diffusion coefficient data[7,12,13] to estimate jump frequency ratios. When this is done, one finds w_0/k_2 must be greater than 2.1 for iron diffusing in copper and greater than 2.9 for iron diffusing in silver. These are reasonable values. They correspond to a repulsion between the impurity and a vacancy which is on the second coordination shell, since an associative jump is less likely than other jumps. This is consistent with Lazarus' screening theory.[14] In this theory, iron is assumed to have a negative excess valence with respect to the noble metals. Since a vacancy also has a negative excess valence, the iron impurity should repel the vacancy.

It is possible that Eq. (25) is not even approximately correct. For example, reduced masses which take into account the other atoms near the impurity probably should be introduced.[15] This could strongly affect the above analysis. Further isotope effect measurements for self-diffusion are needed to clarify this matter. At present though, it appears that Mullen's results can be explained quite reasonably merely by allowing w_0 to be larger than k_2.

B. Drift Mobility

The factor F also appears in the equation for the drift mobility of an ionic impurity in an electric field.[16] As a result, simultaneous determinations of impurity correlation factors and drift mobilities will provide an especially good means of determining F and k_2/w_0.[17] Equation (22) will help in such an analysis.

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