Correlation Effects in Impurity Diffusion

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(Received June 26, 1959)

Expressions are developed giving the correlation factor for an impurity diffusing in an otherwise pure lattice. These expressions will apply in general since, in the derivation, there is no requirement that there must be a large binding energy tending to create vacancy-impurity complexes. When this requirement is eliminated, accurate expressions can be obtained even for the nonclose-packed lattices. Both vacancy and interstitialcy mechanisms are treated. A matrix method developed by LeClaire and Lidiard for the face-centered cubic lattice is applied to various lattices to obtain approximate expressions for the correlation factor. Then a correction is applied giving the effect of those dissociating vacancies (or interstitialcies) which return to the impurity. It is found that the effect is the same as if only a fraction of the dissociative jumps actually occurred. If it is assumed that the effect of an impurity is quite localized, the probability of return can be calculated in a very straightforward manner. It is shown that the effect of returning vacancies (or interstitialcies) can be quite important. The resulting expressions are used to estimate the correlation factor in nondilute alloys.

INTRODUCTION

THE random-walk treatment of diffusion in solids assumes that diffusion takes place by each atom making a succession of elementary atom jumps from site to site throughout the lattice. This process is characterized by a jump frequency ν and a jump distance a, with the resulting expression for the diffusion coefficient D being

$$D = \tfrac{1}{6}a^2\nu. \qquad (1)$$

When the directions of successive atom jumps are related to each other, the usual random-walk treatment must be modified to include the correlation between successive jumps.[1-3] This can be done by multiplying the jump frequency ν by a correlation factor f, with νf being the "effective" jump frequency. In some cases, no correlation between successive jumps will occur; for instance, ordinarily there will be none when diffusion occurs by an interstitial mechanism. However, when diffusion occurs by a vacancy or interstitialcy mechanism, a correlation will occur, thus making it quite a common phenomenon. Conventional diffusion experiments measure only the "effective" jump frequency νf. Thus, in cases where $f \neq 1$, a measurement of the diffusion coefficient will not lead directly to a determination of the jump frequency ν.

This difference between the actual jump frequency ν and the effective jump frequency νf can be quite important. For example, it has been used to explain why (1) the experimentally observed isotope effect for diffusion does not always show the $M^{-\frac{1}{2}}$ dependence predicted by rate theory,[4] and (2) the Einstein relation, σ/D^* $= Ne^2/kT$, relating the ionic conductivity, σ, in ionic crystals to the self-diffusion coefficient, D^*, quite often

is not confirmed experimentally.[5-8] Then, from experiments such as these, one can determine a value for the correlation factor. Since the magnitude of the correlation factor depends on the type of diffusion mechanism, such measurements can help determine the diffusion mechanism in these crystals.[8-10] In case (2) above, when diffusion occurs by an interstitialcy mechanism, an additional correction must be made, since the electric charge moves twice as far during a jump as does each individual atom. This is not a correlation effect as defined above; however, it does allow a further differentiation between the interstitialcy and vacancy mechanisms.

The temperature dependence of the correlation factor can appreciably affect the measured activation energy for diffusion.[11] Also, because of correlation, the dependence of the diffusion coefficient on chemical composition may be quite different from that of the jump frequency. These last two effects will be especially large for fast diffusing impurities.

The correlation factor is related to $\langle \cos\theta \rangle_{\text{Av}}$, the average cosine of the angle between two successive atom jumps.[2] For a vacancy mechanism, where each atom jump is correlated to the immediately preceding jump,

$$f = (1+C)/(1-C), \qquad (2)$$

where $C = \langle \cos\theta \rangle_{\text{Av}}$. With an interstitialcy mechanism,

[1] J. Bardeen and C. Herring, *Atom Movements* (American Society for Metals, Cleveland, 1951), p. 87; *Imperfections in Nearly Perfect Crystals* (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, Discussions Faraday Soc. 23, 105 (1957).
[4] A. H. Schoen, Phys. Rev. Letters 1, 138 (1958).

[5] W. D. Compton, Phys. Rev. 101, 1208 (1956); W. D. Compton and R. J. Maurer, J. Phys. Chem. Solids 1, 191 (1956).
[6] R. J. Friauf, Phys. Rev. 105, 843 (1957).
[7] A. S. Miller and R. J. Maurer, J. Phys. Chem. Solids 4, 196 (1958).
[8] K. Compaan and Y. Haven, Proceedings of the Third International Conference on the Reactivity of Solids, Madrid, April 1956 (unpublished), p. 255; Y. Haven, *Report of the Conference on Defects in Crystalline Solids, Bristol, 1954* (The Physical Society, London, 1955), p. 261.
[9] C. W. McCombie and A. B. Lidiard, Phys. Rev. 101, 1210 (1956).
[10] A. B. Lidiard, Proceedings of the Third International Conference on the Reactivity of Solids, Madrid, 1956 (unpublished), p. 481; *Handbuch der Physik* (Springer-Verlag, Berlin, 1957), Vol. 20, p. 324; Suppl. Nuovo cimento 7, 620 (1958).
[11] J. R. Manning, Phys. Rev. Letters 1, 365 (1958).

TABLE I. Values of $\langle\cos\theta\rangle_{Av}$ and correlation factor f for self-diffusion (after Compaan and Haven[a]).

	$\langle\cos\theta\rangle_{Av}$	f
Vacancy mechanism		
Face-centered cubic lattice	−0.12268	0.78146
Diamond lattice	$-\frac{1}{3}$	$\frac{1}{2}$
Body-centered cubic lattice	−0.15793	0.72722
Simple cubic lattice	−0.20984	0.65311
Interstitialcy mechanism (with collinear jumps)		
Silver chloride lattice	$-\frac{1}{3}$	$\frac{2}{3}$
Face-centered cubic lattice	$-\frac{1}{5}$	$\frac{4}{5}$

[a] See reference 14.

there are two kinds of atom jumps. In one, the atom jumps from a normal lattice site (n) to an interstitial site (i), and, in the other, it jumps from an interstitial site to a normal site. Each $n \rightarrow i$ jump is correlated to the immediately preceding $i \rightarrow n$ jump. However, the direction of the $i \rightarrow n$ jumps are completely independent of any preceding atom jump. Thus, only half of the atom jumps are correlated to previous jumps, and

$$f = 1 + C', \tag{3}$$

where the prime indicates that the average is taken over pairs of consecutive $i \rightarrow n$ and $n \rightarrow i$ jumps only. For both the vacancy and interstitialcy mechanisms, $\langle\cos\theta\rangle_{Av}$ is negative, so, in both cases, f will be less than unity.

In a crystal lattice or sublattice containing just one type of atom, the value of $\langle\cos\theta\rangle_{Av}$ will depend only on the crystal geometry and the diffusion mechanism. These values can in principle be calculated mathematically to as great a precision as desired. Compaan and Haven,[12-14] using an electrical analog, have determined $\langle\cos\theta\rangle_{Av}$ for both vacancy and interstitialcy mechanisms in various types of lattices. Some of these values are listed in Table I. A more extensive list may be found in reference 14.

CORRELATION FACTOR FOR AN IMPURITY ATOM DIFFUSING BY A VACANCY MECHANISM

Face-Centered Cubic Lattice

Lidiard-LeClaire Expression

Lidiard and LeClaire,[2,15] developed an expression for C for an impurity atom which is associated with a neighboring vacancy and is diffusing in an otherwise pure face-centered cubic lattice. They defined three different jump frequencies for the associated vacancy: (1) w_2 is the frequency of exchange with the impurity, (2) w_1 is the frequency of exchange with any one of the four solvent atoms that are common nearest neighbors

[12] K. Compaan and Y. Haven, Trans. Faraday Soc. **52**, 786 (1956).

[13] K. Compaan and Y. Haven, *La Diffusion dans les Metaux* (Bibliotheque Technique Philips, Eindhoven, 1957), p. 19.

[14] K. Compaan and Y. Haven, Trans. Faraday Soc. **54**, 1498 (1958).

[15] A. B. Lidiard, Phil. Mag. **46**, 1218 (1955).

of both the vacancy and impurity, and (3) k_1 is the frequency of exchange with any one of the seven solvent atoms that are nearest neighbors of the vacancy but not of the impurity. It was assumed that all vacancies that made k_1 jumps were completely dissociated from the impurity and, if they returned to the impurity at all, would return from purely random directions. The resulting expression for $C = \langle\cos\theta\rangle_{Av}$ was

$$C = -w_2/(w_2 + 2w_1 + 7k_1). \tag{4}$$

The assumption that all atoms that make k_1 jumps are lost and do not return causes very little error if k_1 is very small compared to w_1 and w_2, but the error becomes larger as k_1 increases.

Contribution from Returning Vacancies

In the present paper, we will calculate the contribution to the correlation factor from the vacancies that return after making k_1 jumps. This will allow consideration of those cases where the impurity is *not* strongly associated with any vacancy.

The general method used will be first to calculate an approximate expression, such as Eq. (4), in which all dissociating vacancies are assumed lost and then modify this equation to correct for the effect of returning vacancies. For the face-centered cubic lattice, the necessary modification is the replacement of $7k_1$, which is the frequency with which a vacancy makes a dissociative jump, by $7Fk_1$ where F is the fraction of dissociating vacancies that effectively do not return. Thus, $7Fk_1$ is the "effective" frequency of dissociative jumps. A similar modification is necessary for other lattices.

A vacancy that has made a k_1 jump can return to any one of the twelve lattice positions on the first coordination shell (nearest neighbors of the impurity). These twelve sites can be divided into five groups, each lying on a different (110) lattice plane. (See Fig. 1.) These groups will be (a) the site from which the k_1 jump originated, (b) the four sites that are nearest neighbors of both site (a) and the impurity, (c) the two sites on the same plane as the impurity, (d) the four nearest neighbor sites on the next parallel plane, and (e) the last nearest neighbor, which will be opposite site (a). We can let the probability that a vacancy which has made a k_1 jump from site (a) will return to the first coordination shell by arriving at a given site (a), (b), (c), (d), or (e) be A, B, C, D, and E, respectively, and let K_1 be the probability that the vacancy, when it jumps from site (a), will make a dissociative jump. For a face-centered cubic lattice, $K_1 = 7k_1/(w_2 + 4w_1 + 7k_1)$. Then, the probability that a vacancy on site (a) will make a dissociative jump and subsequently return to a site (a), (b), (c), (d), or (e) will be K_1A, K_1B, K_1C, K_1D, and K_1E, respectively; and the extra vacancy concentration from the returning vacancies will be given by $K_1(A,4B,2C,4D,E)$, where the coefficients 1, 4, 2, 4, and 1 represent the number of equivalent sites of each type.
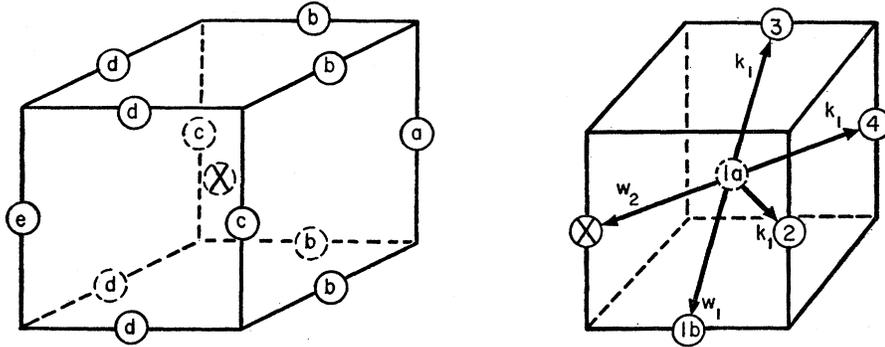
FIG. 1. Face-centered cubic lattice. Nearest neighbors of the impurity X are designated by a, b, c, d, and e. Sites designated 1, 2, 3, and 4 are first, second, third, and fourth nearest neighbors of the impurity. The arrows with w_1, w_2, and k_1 denote the vacancy jump frequencies.

In order to calculate the contribution that the returning vacancies make to $\langle \cos\theta \rangle_{Av}$, we must multiply the extra vacancy concentration by $g \cos\theta$, where g is a constant, giving the probability that the vacancy on its next jump will exchange with the impurity (equal to $w_2/[w_2+4w_1+7k_1]$ for the twelve nearest neighbor sites), and $\cos\theta$ for sites (a) to (e) is given by $(-1, -\frac{1}{2}, 0, \frac{1}{2}, 1)$. The contribution to $\langle \cos\theta \rangle_{Av}$ from the first jump the vacancy makes after returning to the first coordination shell is obviously the same for the actual $K_1(A,4B,2C,4D,E)$ distribution as it would be for a $K_1(A+2B-2D-E, 0, 0, 0, 0)$ distribution. The detailed analysis which follows shows that this is true for all succeeding jumps also.

We can let α_n, β_n, γ_n, δ_n, and ϵ_n be the probabilities that a vacancy which starts at site (a) will be at a given site (a), (b), (c), (d), or (e), respectively, after n jumps, regardless of whether the vacancy makes a dissociative jump or not. These quantities, when summed over n from zero to infinity, give the total probability that the vacancy will visit these sites (multiple visits being counted separately). We can let $\alpha = \sum \alpha_n$, $\beta = \sum \beta_n$, $\gamma = \sum \gamma_n$, $\delta = \sum \delta_n$, and $\epsilon = \sum \epsilon_n$. Then a vacancy which starts at site (a) will have probabilities α, β, γ, δ, and ϵ of visiting a site (a) to (e), respectively; one which starts at a (b) site will have probabilities β, $\alpha+\beta+\gamma+\delta$, $\beta+\delta$, $\beta+\gamma+\delta+\epsilon$, and δ of visiting a site (a) to (e), respectively; one that starts at a (c) site will have probabilities γ, $2\beta+2\delta$, $\alpha+\epsilon$, $2\beta+2\delta$, and γ; one that starts at a (d) site δ, $\beta+\gamma+\delta+\epsilon$, $\beta+\delta$, $\alpha+\beta+\gamma+\delta$, and β; and one that starts at site (e) ϵ, δ, γ, β, and α. From these probabilities and the values of $\cos\theta$, we find that the contribution to $\langle \cos\theta \rangle_{Av}$ from the actual $K_1(A,4B,2C,4D,E)$ distribution is equal to $-gK_1(\alpha+2\beta-2\delta-\epsilon)(A+2B-2D-E)$. This exactly equals the contribution that would be obtained from the equivalent $K_1(A+2B-2D-E, 0, 0, 0, 0)$ distribution.

The equivalent distribution above contains a vacancy concentration only at site (a), with no vacancies being at sites (b), (c), (d), or (e). However, the effect that this equivalent distribution has on $\langle \cos\theta \rangle_{Av}$ is exactly the same as the effect from the actual distribution for returning vacancies. Thus, one can say that a certain

fraction, $F'=A+2B-2D-E$, of the vacancies that make a k_1 (dissociative) jump from site (a) will "effectively" return to this site; and, hence, these vacancies can be treated as if they did not jump at all. A vacancy can make a k_1 jump from any of the twelve sites neighboring on the impurity, but, in each case, the above discussion applies, and the effect on $\langle \cos\theta \rangle_{Av}$ is the same as if only a fraction $F(=1-F')$ of the k_1 jumps actually occurred.

A similar result can also be obtained for other lattices which satisfy the necessary symmetry conditions. In lattices where the only possible impurity jumps are those with $\cos\theta$ equal to $+1$, 0, or -1, the necessary symmetry will always be present. Any lack of symmetry in the jump probabilities merely will make the calculation of the factor F more difficult. For other lattices, the symmetry conditions will be satisfied if (1) the vacancy distribution spreads out symmetrically from the axis determined by the direction of the original vacancy-impurity jump (since then the effect of the actual distribution can be the same as that of a distribution located entirely on this axis) and (2) the impurity jump probabilities (g) are symmetric with respect to this axis. Also, the symmetry conditions could be satisfied if any lack of symmetry in the vacancy distribution were cancelled by an opposite lack of symmetry in g. However, this situation will occur only rarely. Both conditions (1) and (2) above will be satisfied if each impurity jump vector lies along an axis of two- or threefold symmetry. This condition will be satisfied in many crystals; for example, in those with cubic or simple hexagonal lattices. However, in other crystals, such as those with hexagonal-close-packed lattices (especially if $c/a \neq 1.633$), the symmetry conditions will not be fully satisfied.

In a face-centered cubic lattice, the actual frequency of dissociative jumps is given by $7k_1$. However, since not all vacancies that make k_1 jumps are lost, the coefficient of k_1 in Eq. (4) should be multiplied by $F(=1-F')$, the fraction of vacancies making such jumps that "effectively" do not return. Thus,
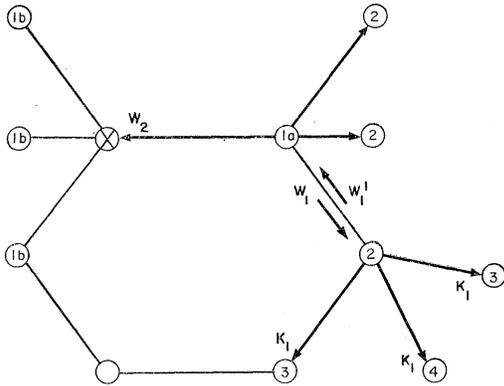
$$C = -w_2/(w_2+2w_1+7Fk_1). \qquad (5)$$

FIG. 2. Diamond lattice (schematic diagram). Nearest neighbors of the impurity X are designated by $1a$ and $1b$. Sites designated 2, 3, and 4 are second, third, and fourth nearest neighbors of the impurity. The arrows with w_2, w_1, w_1', and k_1 denote the vacancy jump frequencies.

It may be noted that only the coefficient of k_1, and not the coefficients of w_1 or w_2, need be modified in order to include the correction for returning vacancies.

The determination of the quantity F can be carried out by a Bardeen-Herring calculation,[1] following the diffusion of the vacancy step by step, eliminating all vacancies that arrive back at nearest neighbor positions, and calculating the probabilities A, B, D, and E by summing over n from one to infinity, where n is the number of vacancy jumps. In general, the results will depend on the vacancy jump frequencies at second nearest neighbor positions and farther from the impurity, and the calculation will be very laborious. However, if the region in the crystal that is disturbed by the impurity atom is quite localized, the jump frequencies for a vacancy at a second nearest neighbor position or farther from the impurity will be very little affected by the presence of the impurity. Then, so long as the vacancy is outside of the first coordination shell, it can be treated as if it were diffusing in a pure lattice. In this case, the problem becomes quite simple, since we can make use of the results obtained by Compaan and Haven for diffusion in a pure lattice.

From Table I, we see that the value of C for self-diffusion by a vacancy mechanism in a face-centered cubic lattice is -0.12268. For self-diffusion, $w_2 = w_1 = k_1$, so from Eq. (5),

$$0.12268 = 1/(3+7F), \qquad (6)$$

and

$$F = 0.7359.$$

When the assumption above is made, this value of F also applies to impurity diffusion, so

$$C = -w_2/(w_2 + 2w_1 + 5.151k_1), \qquad (7)$$

and, from Eq. (2), the correlation factor is given by

$$f = (2w_1 + 5.151k_1)/(2w_2 + 2w_1 + 5.151k_1). \qquad (8)$$

Diamond Lattice

The method described above can also be used to determine the correlation factor for diffusion of an impurity in a diamond lattice. Since an approximate expression analogous to Eq. (4), assuming that all vacancies that make dissociative jumps are lost, is not available for the diamond lattice, it will first be necessary to develop one. Then we will make a correction for those vacancies that return.

In the face-centered cubic lattice, the vacancy can exchange with a solvent atom without dissociating from the impurity; and if the vacancy is tightly bound to the impurity (giving $w_1 \gg k_1$), the approximate expression should be quite accurate. However, in the diamond lattice, this is not so. Thus, in this lattice (and other nonclose-packed lattices), it is essential to consider the effect of returning vacancies if one desires an accurate expression.

We can begin by assigning vacancy jump frequencies (see Fig. 2), letting w_2 be the frequency of exchange of a vacancy with a neighboring impurity atom, w_1 be the frequency with which a vacancy will jump from a position as nearest neighbor to an impurity to a next nearest neighbor position, w_1' be the frequency with which a vacancy will make a jump from a position as a next nearest neighbor of an impurity to a nearest neighbor position (the reverse of a w_1 jump), and k_1 be the frequency with which a vacancy will jump from a given position in the second coordination shell of the impurity (next nearest neighbor) to one on the third coordination shell (third or fourth nearest neighbor). As a first approximation, we will consider vacancy motion on only the first and second coordination shells; that is, on those lattice points that can be reached in one or two jumps away from the impurity. All vacancies that reach the third coordination shell (by making k_1 jumps) will be considered lost.

An approximate expression for C can then be obtained by applying a method similar to that used by LeClaire and Lidiard[2] for the face-centered cubic lattice. Let us consider an impurity atom that has just exchanged positions with a vacancy. Then let $p_n(s)$ be the probability that site s, a nearest neighbor of the impurity site, will be occupied by the vacancy after the nth succeeding vacancy jump. If $\tau(s)$ is the contribution to $\langle \cos\theta \rangle_{Av}$ by the next jump of the vacancy from site s (equal to g, the probability of exchange with the impurity, multiplied by the appropriate $\cos\theta$),

$$C = \sum_{n=0}^{\infty} \sum_{\text{all } s} \tau(s) p_n(s). \qquad (9)$$

By ordering the sites in some suitable manner, the various $p_n(s)$ coefficients can be written as a column matrix p_n and the $\tau(s)$ can be written as a row matrix τ. Because of lattice symmetries, some elements of these matrices will always be equal to each other, so both p_n
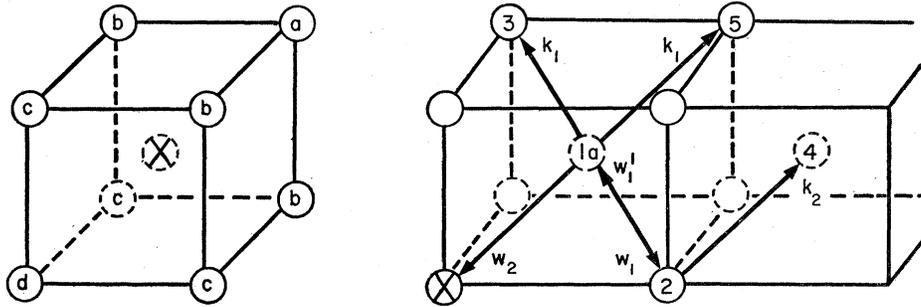
FIG. 3. Body-centered cubic lattice. Nearest neighbors of the impurity X are designated by a, b, c, and d. Sites designated 1, 2, 3, 4, and 5 are first, second, third, fourth, and fifth nearest neighbors of the impurity. The arrows with w_2, w_1, w_1', k_1, and k_2 denote the vacancy jump frequencies.

and τ can be contracted. Then, each element in the contracted τ matrix will contain an additional factor giving the number of equivalent sites represented by that element. In the case of the diamond lattice, the position occupied by the vacancy immediately after the impurity-vacancy exchange will correspond to $\cos\theta = -1$. The other three positions neighboring on the impurity will be equivalent, each corresponding to $\cos\theta = \frac{1}{3}$. Thus, the τ matrix is given by

$$\tau = g(-1, 1),\qquad (10)$$

where $g = w_2/(w_2 + 3w_1)$.

A vacancy that begins a random walk at one of the four positions neighboring on the impurity can return to this or another such position only after an even number of jumps. Therefore, we need to calculate p_n only when n is even. The probability coefficients $p_{n+2}(s)$ are related to the $p_n(s)$ by a set of linear equations, so, in matrix notation,

$$p_{n+2} = P p_n,\qquad (11)$$

where P is the square matrix,

$$P = h\begin{bmatrix} 3 & 0 \\ 0 & 3 \end{bmatrix},\qquad (12)$$

with

$$h = \left(\frac{w_1'}{w_1' + 3k_1}\right)\left(\frac{w_1}{w_2 + 3w_1}\right).$$

Vacancy paths that involve an exchange with the impurity atom have been neglected in calculating P above, since we are interested only in finding the cosine of the angle between two successive *impurity* jumps.

From Eqs. (10) and (12),

$$\tau P = 3h\tau,\qquad (13)$$

and

$$\tau P^n = (3h)^n \tau.\qquad (14)$$

From Eqs. (9) and (11),

$$C = \tau \sum_{n=0}^{\infty} P^n p_0,\qquad (15)$$

where p_0 is the column matrix $\{1,0\}$. Thus,

$$C = -g(1 - 3h)^{-1},\qquad (16)$$

$$C = -w_2/\{w_2 + [9w_1 k_1/(w_1' + 3k_1)]\}.\qquad (17)$$

However, this is only an approximate value since the effect of the return of dissociating vacancies has been neglected.

A certain fraction of the vacancies that make k_1 jumps will eventually return. As in the face-centered cubic lattice, the effect of vacancies which have escaped by making a k_1 jump from site α (which in the case considered here will be on the second coordination shell) returning to one of the twelve lattice sites on this shell will be the same as if a fraction $(1 - F)$ returned to site α. A returning vacancy cannot reach the first coordination shell in the diamond lattice without passing through the second coordination shell. Thus, so long as a vacancy in the third coordination shell or farther from the impurity diffuses as if it were in a pure lattice, the probabilities of return will be the same as for self-diffusion. From Table I, we find $C = -\frac{1}{3}$ for self-diffusion in a diamond lattice. For self-diffusion, $w_2 = w_1 = w_1' = k_1$, so, from Eq. (17),

$$\tfrac{1}{3} = 1/\{1 + [9F/(1 + 3F)]\},\qquad (18)$$

and $F = \frac{2}{3}$.

Thus, for an impurity diffusing by a vacancy mechanism in an otherwise pure diamond lattice, the correlation factor is given by

$$f = 3w_1 k_1/[w_2(w_1' + 2k_1) + 3w_1 k_1].\qquad (19)$$

If $k_1 = w_1'$, i.e., if the direction of jump of a vacancy in the second coordination shell is random, we obtain the very simple expression,

$$f = w_1/(w_2 + w_1).\qquad (20)$$

Body-Centered Cubic Lattice

The preceding arguments can be extended to the body-centered cubic lattice. (See Fig. 3.) As in the diamond lattice, a vacancy cannot move directly from one position neighboring on an impurity to another;

however, unlike the diamond lattice, not all sites on the second coordination shell are equivalent, since second, third, and fifth nearest neighbors all lie on this shell. Hence, the simple treatment used for the diamond lattice will not be adequate.

We can assign vacancy jump frequencies, letting w_2 be the frequency of exchange of a vacancy with a neighboring impurity atom, w_1 be the frequency of jump from one of the nearest neighbor sites to one of the second nearest neighbor sites, w_1' be the frequency of jump from a second to a first nearest neighbor site (the reverse of a w_1 jump), k_1 be the frequency of jump from a nearest neighbor position to one of the third or fifth nearest neighbor positions, k_2 be the frequency of jump from a second to one of the fourth nearest neighbor positions, and all other jump frequencies be w_0, the vacancy jump frequency in pure solvent.

The first nearest neighbor sites can be divided into four groups, (a) one site at (111), (b) three sites at $(11\bar{1})$, (c) three sites at $(1\bar{1}\bar{1})$, and (d) one site at $(\bar{1}\bar{1}\bar{1})$ with the corresponding cosines -1, $-\frac{1}{3}$, $\frac{1}{3}$, 1. Thus,

$$\tau = g(-1, -1, 1, 1), \qquad (21)$$

where $g = w_2/(w_2 + 3w_1 + 4k_1)$.

As a first approximation, we will consider the motion of vacancies on the first and second coordination shells only. Then,

$$p_{n+2} = Pp_n, \quad \text{where} \quad P = P_1 + P_2. \qquad (22)$$

Here, P_1 refers to cases where the first vacancy jump is a w_1 jump, while P_2 refers the cases where it is a k_1 jump. Then,

$$P_1 = h_1 \begin{bmatrix} 3 & 6 & 3 & 0 \\ 2 & 5 & 4 & 1 \\ 1 & 4 & 5 & 2 \\ 0 & 3 & 6 & 3 \end{bmatrix}, \qquad (23)$$

and

$$P_2 = h_2 \begin{bmatrix} 4 & 3 & 0 & 0 \\ 1 & 4 & 2 & 0 \\ 0 & 2 & 4 & 1 \\ 0 & 0 & 3 & 4 \end{bmatrix}, \qquad (24)$$

with

$$h_1 = \frac{w_1'}{4w_1' + 4k_2} \times \frac{w_1}{w_2 + 3w_1 + 4k_1},$$

and

$$h_2 = \frac{1}{8} \frac{k_1}{w_2 + 3w_1 + 4k_1}.$$

From Eqs. (21) through (24),

$$\tau P = (4h_1 + 5h_2)\tau, \qquad (25)$$

and using Eq. (15) with $p_0 = \{1,0,0,0\}$, we find

$$C = \frac{-w_2}{w_2 + 2w_1 + 3.375k_1 + [w_1 k_2/(w_1 + k_2)]}. \qquad (26)$$

The fraction of vacancies that effectively do not return after making a k_2 jump will be different from the fraction that effectively do not return after making one of the dissociative jumps which can follow a k_1 jump. Also, these fractions will depend on the jump frequencies w_1' and k_2, so they cannot be calculated easily; however, they both should be ~ 0.6.

If we assume $w_1' = k_2 = w_0$, and consider a vacancy as being dissociated after making either a k_1 jump or a w_1 jump, we obtain the alternate expression,

$$C = -w_2/(w_2 + 3F_1 w_1 + 4F_2 k_1), \qquad (27)$$

where F_1 and F_2 are the fraction of vacancies making w_1 and k_1 jumps that are effectively lost.

We still cannot solve for F_1 and F_2 in Eq. (27) by the simple method used for the face-centered cubic and diamond lattices. However, the vacancy will diffuse as in a pure lattice until it returns to a nearest neighbor position, so a calculation by the Bardeen-Herring method[1] (or the Compaan-Haven electrical analog method[12]) presents no great difficulties. The step involving elimination of all vacancies that return to a nearest neighbor position can be neglected if, at the end of the calculation, a simple correction is made for those vacancies that return more than once. The fractions F_1 and F_2 were calculated by the Bardeen-Herring method. The contributions from $n \leq 9$ were summed exactly, while those from $n > 9$ were integrated, using the expression,

$$\begin{array}{l} \text{concentration} \\ \text{of vacancies} \end{array} \propto n^{-\frac{3}{2}} \exp\left[-\frac{6r^2}{4na^2}\left(\frac{n-1}{n}\right) - \frac{3}{4n} \right], \qquad (28)$$

expanded in inverse powers of n. In this expression, n is the number of vacancy jumps, a is the jump distance, and r is distance from the origin. The resulting values were $F_1 = 0.783$ and $F_2 = 0.746$, with the error being limited to the third significant figure.

Even for fairly large values of n, there is a considerable effect from the inclusion of the quantities $(n-1)/n$ and $(3/4n)$ in Eq. (28). However, the other higher order terms that one obtains in the random walk derivation of Eq. (28) can be neglected.
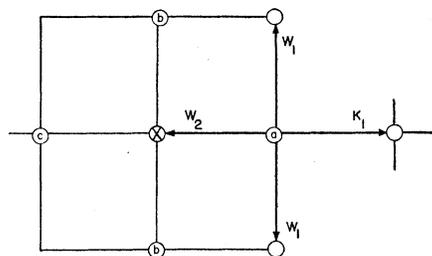

FIG. 4. Simple cubic lattice. Nearest neighbors of the impurity X are designated by a, b, and c. The arrows with w_2, w_1, and k_1 denote the vacancy jump frequencies.
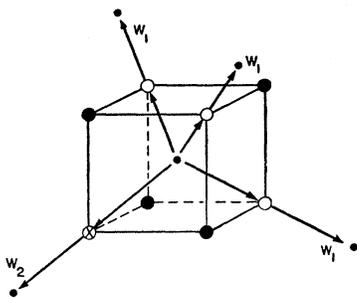
FIG. 5. Silver chloride lattice. Interstitialcy mechanism with collinear jumps. The small black dots denote the possible interstitial positions. The large black dots denote the Cl ion lattice sites and the open circles the Ag ion lattice sites. The impurity is marked with an X. The arrows with w_1 and w_2 denote the interstitialcy jump frequencies.

Quite accurate results can be obtained from the procedure described above, i.e., summing the contributions from the smaller values of n and then using Eq. (28) to integrate over the larger values of n. For comparison, the values of $\langle\cos\theta\rangle_{Av}$ for various pure lattices were calculated by this method, assuming diffusion by both vacancy and interstitialcy mechanisms. For diffusion by vacancies, the results agreed to four significant figures with the most recent Compaan-Haven values.[14] Similar calculations for diffusion by interstitialcies gave agreement to two or three significant figures. The probability distribution for a vacancy that has caused a tracer jump (giving the possible positions of this vacancy at some later time) will spread out symmetrically from the original tracer position; while that for an interstitialcy will not. This makes the calculations for a vacancy mechanism both easier and more precise than those for an interstitialcy mechanism.

Simple Cubic Lattice

The treatment for a simple cubic lattice (see Fig. 4) is quite similar to that for the body-centered cubic. If w_2 is the frequency with which a vacancy exchanges with a neighboring impurity, w_1 is the frequency with which a vacancy will jump from a nearest neighbor position to one of the next nearest neighbor positions, k_1 is the frequency from a nearest neighbor position to the fourth nearest neighbor position, and all other jump frequencies are the same as in a pure lattice,

$$C = -w_2/(w_2+4F_1w_1+F_2k_1). \qquad (29)$$

A Bardeen-Herring calculation shows that $F_1=0.760$ and $F_2=0.726$, with the error again being limited to the third significant figure.

CORRELATION FACTOR FOR AN IMPURITY ATOM DIFFUSING BY AN INTERSTITIALCY MECHANISM

AgCl Lattice

In AgCl[5,9] and AgBr,[6,7] it is believed that silver diffusion occurs at least in part by means of an inter-

stitialcy mechanism. For the collinear case, where the interstitial atom and the normal lattice atom that it displaces both move in the same direction during the interstitialcy jump, the interstitial positions will lie on a diamond-like lattice. (See Figs. 5 and 2.) The analysis for interstitialcy diffusion in an AgCl lattice is very similar to that for vacancy diffusion in a diamond lattice, and the same value of $\langle\cos\theta\rangle_{Av}$ is obtained. Finally, if $k_1=w_1'$, the correlation factor is given by

$$f = 2w_1/(w_2+2w_1). \qquad (30)$$

This last expression differs from that for vacancy diffusion in a diamond lattice because the relation between f and $\langle\cos\theta\rangle_{Av}$ is different. [See Eq. (2) and (3).]

Face-Centered Cubic Lattice

In a face-centered cubic lattice in which interstitialcy diffusion occurs by means of collinear jumps, the interstitial positions will lie on a simple cubic lattice. (See Fig. 6). If w_2 is the frequency with which an interstitial atom will jump to a lattice site by pushing a neighboring impurity from that site, and w_1 is the corresponding frequency for a neighboring solvent atom, we obtain

$$C = -w_2/(w_2+5Fw_1), \qquad (31)$$

where F is the fraction of interstitialcies that are effectively lost after a w_1 jump. From Table I, $C=-0.200$ for self-diffusion. Thus, $F=0.8$; and the correlation factor f is given by

$$f = 4w_1/(w_2+4w_1). \qquad (32)$$

If we distinguish between the four w_1 jumps which are at right angles to the direction of the original impurity jump, calling these k_1 jumps, and the one w_1 jump that is in the same direction as the original impurity jump, calling this a k_2 jump, we obtain

$$C = -w_2/(w_2+4F_1k_1+F_2k_2). \qquad (33)$$

From a Bardeen-Herring calculation, it is found that $F_1=0.815$ and $F_2=0.740$, with the last figure being estimated.
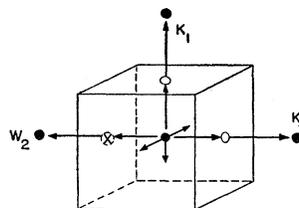

FIG. 6. Face-centered cubic lattice. Interstitialcy mechanism with collinear jumps. The small black dots denote the possible interstitial positions. The open circles denote the normal lattice sites. The impurity is marked with an X. The arrows with w_2, k_1, and k_2 denote the interstitialcy jump frequencies.

CORRELATION FACTOR FOR DIFFUSION IN ALLOYS

If a few simplifying assumptions are made, the preceding analyses can be extended to the case of nondilute alloys. For example, let us consider diffusion by a vacancy mechanism in a face-centered cubic substitutional alloy.

In the nondilute range, there will be a large number of impurity atoms, so a vacancy should not be bound strongly to any one of them and also w_1 should be approximately equal to k_1. Effects from fluctuations in the local concentration of impurity atoms should average out, so, on the average, $w_1 = k_1 = W$, where W is the average jump frequency for a vacancy. In a binary alloy having N_A atom fraction of A atoms and N_B atom fraction of B atoms,

$$W = N_A w_A + N_B w_B, \qquad (34)$$

where w_A and w_B are the frequencies with which a vacancy exchanges with a neighboring A or B atom. Then, from Eq. (8), the correlation factor f_A for A atoms is given by

$$f_A = 7.151W/(2w_A + 7.151W), \qquad (35)$$

and a similar expression holds for B atoms.

The correlation factor will be a function of chemical composition, since, in general, both W and w_A will depend on N_A and N_B. When only a small amount of the faster diffusing species is present, the variation with composition can be quite large,[16] since, in this case, a small change in composition can cause a relatively large change in W. In both dilute[11] and nondilute[16] alloys the correlation factor can be expected to depend on temperature. This dependence will tend to be greatest when the faster diffusing species is present in dilute concentration. In general, because of the w_A dependence, all correlation effects will be larger for the faster diffusing species.

DISCUSSION

A theory has been developed to predict correlation effects for impurity diffusion and diffusion in nondilute alloys in various crystal lattices. The method is quite general and can be extended to many lattices not treated here. For diffusion of an impurity atom in an otherwise pure lattice, it was assumed that motion of the vacancy or interstitialcy when it is outside the first or second coordination shell is the same as in a pure crystal. This assumption should not introduce any large error and allows a considerable simplification. In nondilute alloys, the assumption that the effect of a tracer atom is quite localized seems very reasonable. Then, if it is assumed that fluctuations in local composition will not greatly affect the average correlation factor, an expression for the correlation factor can be derived directly from that for impurity diffusion.

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[16] J. R. Manning, Phys. Rev. **116**, 69 (1959).

TABLE II. Correlation factors for diffusion by a vacancy mechanism in a face-centered cubic alloy. In Column A, the effect of returning vacancies is included; while in Column B, it is not. [See Eqs. (2), (4), and (35).]

w_2/W	Column A $f = 7.151W/(2w_2 + 7.151W)$	Column B $f = 9W/(2w_2 + 9W)$
0.2	0.947	0.957
1.0	0.781	0.818
5.0	0.417	0.474
25.0	0.125	0.153

In the derivation of these expressions, the probability of a dissociated vacancy (or interstitialcy) returning to the impurity was considered. The effect of the returning vacancy (or interstitialcy) quite often will not be negligible. Table II shows the effect in the case of vacancy diffusion in a face-centered cubic nondilute alloy.

The face-centered cubic lattice will show the smallest effect from returning vacancies, since in this lattice it is possible for the vacancy to exchange with a solvent atom without dissociating from the impurity. If the vacancy is tightly bound to the impurity, the approximate expression [Eq. (4)] should be quite accurate. In the other lattices considered, this is not so. In these cases, if we neglected the possibility that a vacancy which has dissociated from the impurity by jumping to a non-nearest neighbor position may return, only the first term in the Bardeen-Herring series[1] [see Eq. (9)] would remain. Then C would equal g, the probability that after an atom has jumped it will immediately re-exchange places with the vacancy. This would be a poor approximation, as may be seen from Table III, which shows values of the correlation factor, both corrected and uncorrected for returning vacancies, for an impurity diffusing in a diamond lattice.

Extending the region in which the vacancy and impurity are considered associated to include next nearest neighbors [as in Eq. (17)] will appreciably reduce both the effect from dissociating vacancies and the error from the assumption that the effect of the impurity is very localized. However, this will usually make the treatment much more complicated. For example, compare Eqs. (26) and (27) in the body-centered cubic case.

Even in the face-centered cubic lattice, the effect of returning vacancies can be quite large. Let us consider an impurity atom B diffusing by a vacancy mechanism in a face-centered cubic lattice of A atoms. The diffusion coefficient D_B of the impurity will be related to the diffusion coefficient D_A for A atoms diffusing in pure A by the equation,

$$\frac{D_B}{D_A} = \frac{f_B}{f_A} \frac{w_2}{w_0} \exp(E_B/kT), \qquad (36)$$

where f_A and f_B are the correlation factors, w_2 the frequency of exchange of a vacancy with a neighboring impurity atom, w_0 the frequency of exchange of a

TABLE III. Correlation factors for impurity diffusion by a vacancy mechanism in a diamond lattice. In Column A the effect of returning vacancies is included; while in Column B, it is not. [See Eqs. (2), (10), and (20).]

w_2/w_1	Column A $f = w_1/(w_2 + w_1)$	Column B $f = 3w_1/(2w_2 + 3w_1)$
0.2	0.833	0.882
1.0	0.500	0.600
4.0	0.200	0.273
16.0	0.059	0.089
∞	w_1/w_2	$1.5\,w_1/w_2$

vacancy in a pure lattice with a given neighboring A atom, E_B the binding energy between a vacancy and an impurity, k Boltzmann's constant, and T the absolute temperature.

To take an extreme example, let us assume that there is no binding energy and that the jump frequencies w_1 and k_1 in Eqs. (5) and (8) are equal to w_0. If the correction for returning vacancies is included [Eq. (8)],

$$f_B = 7.151w_0/(2w_2 + 7.151w_0). \qquad (37)$$

From Table I, $f_A = 0.7815$, so in the limiting case where $w_2/w_0 \to \infty$, we find $D_B/D_A \to 4.58$. If the correction for returning vacancies is not included in calculating f_B, we find $D_B/D_A \to 5.76$. A typical experimental value of D_B/D_A is 4.0. With this value of D_B/D_A, Eq. (36) in the corrected case gives $w_2/w_0 = 24.7$; while in the uncorrected case it gives $w_2/w_0 = 10.2$. This is a considerable difference.

Usually the effect will be smaller than in the case considered above. For example, calculations assuming an appreciable binding energy and letting w_1 equal w_2 give considerably smaller values of w_2/w_0 and show only a small effect from consideration of returning vacancies. However, the correction is easy to apply, and it would seem desirable, in all cases, to use the corrected expressions. This is especially true in the non-close-packed lattices.

Accurate measurements of the correlation factor could contribute greatly to the understanding of diffusion phenomena. Atomistic theories of diffusion, such as those of Zener,[17] Lazarus,[18] Swalin,[19] Overhauser,[20] and Rice,[21] attempt to determine the atom jump frequencies. Accurate measurements of the correlation factor would be very useful in comparing these theories with experiment, since (1) the correlation factor f must be included in Eq. (1), relating the diffusion coefficient to the jump frequency, and (2) the expression for the correlation factor itself will involve the jump frequencies. Accurate isotope effect experiments should allow an estimation of the correlation factor. (It may be noted that comparison of the ionic conductivity with the tracer diffusion coefficient in ionic crystals will *not* allow the calculation of the correlation factor for an *impurity*.) Experimental values for the correlation factor can then be compared with expressions such as those derived in the present paper to estimate the values of the jump frequencies near an impurity. For diffusion by a vacancy mechanism, the diamond lattice presents the simplest geometry, with the face-centered cubic lattice being next in simplicity.

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