Random-Walk Method for Calculating Correlation Factors: Tracer Diffusion by Divacancy and Impurity-Vacancy Pairs in Cubic Crystals

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The random-walk technique is extended in a way that allows correlation factors to be calculated in all cases where principle axes for diffusion can be found. The results are applicable both to tracer and to impurity diffusion. Explicit calculations are given of correlation factors for the diffusion of tracers by bound impurity-vacancy pairs in fcc metals and NaCl-type ionic crystals, and by bound divacancy pairs in NaCl-type ionic crystals, CsCl-type ionic crystals, and fcc metals. Appropriate modifications for the "isotope effect" are made for the case of impurity-vacancy pairs.

1. INTRODUCTION

AS defined by Bardeen and Herring,[1] the correlation factor f is the ratio of the diffusion coefficient of a species to the diffusion coefficient computed on the assumption of randomly oriented jump vectors. In general, f is less than unity because, in general, successive jumps of a particle tend to have displacements in opposite directions. This is obviously the case for diffusion by a vacancy mechanism: a tracer having exchanged with a vacancy has a better than random chance of executing the reverse jump.

Lately, there has been much experimental and theoretical effort in the determination of correlation factors for self- and for impurity-diffusion in various classes of crystals and for various diffusion mechanisms. References to particular work may be found in the review articles by Friauf[2] and by Howard and Lidiard.[3] Generally, the correlation factor plays one of two roles ni the investigation of the atomic mechanisms of diffusion. If the diffusion mechanism is known, then a comparison of measured and calculated values of the correlation factor may allow certain atomic parameters (e.g., jump frequencies) to be determined. On the other hand, when there is some uncertainty about whether diffusion occurs by one or another mechanism, the question may sometimes be decided by a comparison of the measured correlation factor with those implied by the alternative diffusion models. It was demonstrated in this way that silver interstitials in AgBr and AgCl diffuse by the so-called "interstitialcy" mechanism.[2]

Two general methods have been available to calculate correlation factors. In the pair-association method,[3-5] impurity-vacancy (or tracer-vacancy) pairs are distinguished and their flux calculated in terms of a set of frequencies describing vacancy jumps between sites variously situated with respect to the impurity. Pair-association calculations proceed by straight-forward kinetic methods and yield closed-form expressions for diffusion coefficients and hence for correlation factors. However, the approximations which are inherent in this type of calculation make it somewhat inaccurate unless there is substantial binding between the vacancy and the impurity. Also, it appears that the pair-association method can be easily applied only to the case of diffusion by a single-vacancy mechanism in cubic crystals.

In the random-walk method, introduced by Bardeen and Herring,[1] the starting point is the Einstein formula

$$D = \langle R^2 \rangle / 6t, \qquad (1.1)$$

(or a suitable generalization of this formula for an anisotropic crystal). Here $\langle R^2 \rangle$ is the mean-square displacement of a diffusing particle in the time t. If the displacement vector $\mathbf{R}$ of the diffusing particle is written as the sum of the vectors representing individual particle jumps, then the correlation factor may be found as an infinite series in the cross terms between jump vectors [cf. Eq. (2.4)]. In situations having special symmetry, namely situations where all jump vectors of the diffusing particle are axes of two- or threefold symmetry,[6,7] the series expression for the correlation factor reduces to the simple expression

$$f = [1 + \langle \cos\theta_{12} \rangle / 1 - \langle \cos\theta_{12} \rangle], \qquad (1.2)$$

where $\langle \cos\theta_{12} \rangle$ is the average value of the cosine of the angle between any two consecutive jumps of the diffusing atom. The quantity $\langle \cos\theta_{12} \rangle$ may be calculated numerically.[6,8] We note, however, that the validity of Eq. (1.2) depends on a rather strict symmetry condition. The use of the random-walk method has been, for the most part, limited to cases where such a condition is satisfied. (Exceptions are the particular calculations of Compaan and Haven,[6] of Mullen[9] and of Huntington and Ghate.[10])

[1] J. Bardeen and C. Herring, in *Imperfections in Nearly Perfect Crystals*, edited by W. Shockley (John Wiley & Sons, Inc., New York, 1952), p. 261.

[2] R. J. Friauf, J. Appl. Phys. Suppl. 33, 494 (1962).

[3] R. E. Howard and A. B. Lidiard, Rept. Progr. Phys. 27, 161 (1964).

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

[5] R. E. Howard and A. B. Lidiard, J. Phys. Soc. Japan Suppl. 11 18, 197 (1963).

[6] K. Compaan and Y. Haven, Trans. Faraday Soc. 52, 786 (1956); 54, 1498 (1958).

[7] An equivalent but somewhat different version of this symmetry condition is presented in Sec. 2.

[8] J. R. Manning, Phys. Rev. 136, A1758 (1964), and references therein.

[9] J. G. Mullen, Phys. Rev. 124, 1723 (1961).

[10] H. B. Huntington and P. B. Ghate, Phys. Rev. Letters 8, 421 (1962); H. B. Huntington, P. B. Ghate, and J. H. Rosolowski, J. Appl. Phys. 35, 3027 (1964).

One of the objects of this paper is to extend the random-walk method by deriving an equation for the correlation factor, analogous to Eq. (1.2), which remains valid irrespective of the symmetry of the jump vectors. Such an equation is derived in Sec. 2 and permits correlation factors to be calculated in cases where Eq. (1.2) is not applicable, by the same computational methods as for simpler cases, and without very much greater difficulty. In Sec. 3, we calculate correlation factors for the particular cases of tracer diffusion by divacancy pairs and by impurity-vacancy pairs in cubic metals and ionic crystals (impurity-vacancy pairs in fcc metals and NaCl-type ionic crystals; divacancy pairs in fcc metals, NaCl-type ionic crystals and CsCl-type ionic crystals). In addition, for the case of impurity-vacancy pairs, we calculate the effect on the correlation factor of varying the mass of the tracer.

There has been much evidence lately for the operation of pair mechanisms in certain situations[2,11-14] and the correlation factors associated with these mechanisms may soon be measured. It is hoped that the present calculations may serve as a basis for obtaining detailed information from such measurements, particularly information about the ratios of certain characteristic vacancy-jump frequencies which determine the correlation factor (e.g., the ratio of the impurity-vacancy exchange frequency to that for a normal atom-vacancy exchange if the diffusion mechanism is via impurity-vacancy pairs).

2. FORMULA FOR THE CORRELATION FACTOR

We shall obtain a generalization of Eq. (1.2) by extending the formulation of the random-walk method due to Mullen.[9,15] We begin by writing the Einstein formula in a manner valid for anisotropic crystals. For an anisotropic crystal, the diffusion coefficient is, in general, a second-rank tensor. Such a tensor may be diagonalized by finding principle axes for diffusion and we assume in what follows that such axes have been found. In many cases, they may be found by inspection but in cases of sufficient complexity their determination may not be straightforward. Assuming that the diffusion-coefficient tensor has been diagonalized it is easy to show that each of the diagonal elements, D_{xx} for example is given by an equation of the form

$$D_{xx} = \lim_{t \to \infty} \langle X^2 \rangle / 2t, \quad (2.1)$$

[11] N. Laurence, Phys. Rev. **120**, 57 (1960); K. Tharmalingam and A. B. Lidiard, Phil. Mag. **6**, 1157 (1961).
[12] L. W. Barr and A. D. LeClaire, Proc. Brit. Ceramic Soc. **1**, 109 (1964).
[13] L. W. Barr, J. A. Morrison, and P. A. Schroeder, J. Appl. Phys. **36**, 624 (1965).
[14] F. Ramsteiner, G. Lampert, A. Seeger, and W. Schule, Phys. Status Solidi, **8**, 863 (1965).
[15] The results of this section were reported on at the *Fifth Conference on the Reactivity of Solids, Munich, 1964*, edited by G.-M. Schwab (Elsevier Publishing Company, Amsterdam, 1965), p. 255.

where $\langle X^2 \rangle$ is the mean-square displacement of a diffusing particle along the x principle axis in the time t. If the crystal is isotropic, $\langle X^2 \rangle = \langle \gamma^2 \rangle = \langle Z^2 \rangle = \frac{1}{3}\langle R^2 \rangle$, and we recover Eq. (1.1).

Following Mullen we rewrite Eq. (2.1) in terms of individual atomic jumps. Suppose that in the time t there is a sequence of n jumps and suppose that x_i is the projection of the ith jump along the principal axis x. (The magnitude of x_i may be positive, negative, or zero.) We may then write for the total displacement X along this axis

$$X = \sum_{i=1}^{n} x_i. \quad (2.2)$$

Substituting Eq. (2.2) into Eq. (2.1) we find that

$$D_{xx} = \lim_{n \to \infty} \langle (\sum_{i=1}^{n} x_i)^2 \rangle / 2t(n)$$

$$= \lim_{n \to \infty} f_x \langle (\sum_{i=1}^{n} x_i^2) \rangle / 2t(n), \quad (2.3)$$

where we define the correlation factor f_x, for the x principle axis, as

$$f_x = 1 + 2 \sum_{i=1}^{\infty} \langle x_i x_{i+1} + x_i x_{i+2} + \cdots \rangle / \sum_{i=1}^{\infty} \langle x_i^2 \rangle. \quad (2.4)$$

We note that in evaluating Eqs. (2.3) or (2.4) we need only include those jumps for which the x component of displacement is nonzero and we here and henceforth in this section restrict our considerations to such jumps. In the absence of any correlations between jumps (i.e., if the probability that the jump j is of a particular length and direction is independent of the length and direction of the preceding jump $j-1$, for all j) then

$$\langle x_j x_{j+k} \rangle = \langle x_j \rangle \langle x_{j+k} \rangle = 0,$$

for all j and $j+k$. Hence, in this case, $f_x = 1$.

Equation (2.4) for f_x is in a somewhat intractable form since it involves correlations not only between consecutive jumps (i.e., terms $\langle x_j x_{j+1} \rangle$), but also correlations between jumps that are not consecutive (i.e., terms $\langle x_j x_{j+k} \rangle$, $k>1$). We wish now to reduce Eq. (2.4) to a form where only terms describing consecutive jumps appear. The simplest, nontrivial case where such a reduction can be made is the case where all jumps are equivalent; i.e., for all jumps j which have nonzero projections along the x axis, the magnitudes of the projections $|x_j|$ are the same and also the averages $\langle x_j x_{j+1} \rangle$ are the same. This is the case, for eample, for diffusion of tracers by vacancies in a cubic crystal. Here, all nonvanishing projections of tracer jumps in the x direction (which we take along a $\langle 100 \rangle$ axis) are of the same length, a, the spacing between lattice planes; also the probability that the x projections of two consecutive tracer jumps are in the same direction or in opposite

directions is the same for any two consecutive jumps. Hence

$$\langle x_j x_{j+1} \rangle / a^2 = \xi, \tag{2.5}$$

where ξ is a constant independent of j. When all jumps are equivalent[6,9]

$$\frac{\langle x_j x_{j+2} \rangle}{a^2} = \frac{\langle x_j x_{j+1} \rangle}{a^2} \frac{\langle x_{j+1} x_{j+2} \rangle}{a^2} = \left(\frac{\langle x_1 x_2 \rangle}{a^2} \right)^2. \tag{2.6}$$

By induction

$$\langle x_j x_{j+i} \rangle / a^2 = (\langle x_1 x_2 \rangle / a^2)^i. \tag{2.7}$$

Equation (2.7) now allows Eq. (2.4) to be summed, and we obtain

$$f_x = [1 + \langle x_1 x_2 \rangle / a^2 / 1 - \langle x_1 x_2 \rangle / a^2], \tag{2.8}$$

which expresses the correlation factor in terms of an average over any two consecutive particle jumps. If the crystal is isotropic, then it is easy to show that $\langle x_1 x_2 \rangle / a^2 = \langle \cos\theta_{12} \rangle$, the average of the cosine of the angle between any two consecutive jump vectors, and we recover Eq. (1.2).

We wish now to find the analog of Eq. (2.8) under the general condition that not all jumps are equivalent. Let us suppose quite generally that there are N types of jumps (labeled by the subscripts $\alpha = 1, \cdots, N$) such that for all x_j of the same type the series

$$\sum_{i=1}^{\infty} \langle x_j x_{j+i} \rangle = \sum_{i=1}^{\infty} \langle x_\alpha x_{\alpha,i} \rangle,$$

where the subscript α, i refers to the ith jump following a jump of type α. If we assume that all nonzero x displacements are of the same length a, (this restriction will later be removed) then we may write Eq. (2.4) as

$$f_x = 1 + 2 \sum_{\alpha=1}^{N} c_\alpha \sum_{i=1}^{\infty} \langle x_\alpha x_{\alpha,i} \rangle / a^2, \tag{2.9}$$

where c_α is the fraction of jumps of type α in any long sequence of jumps [i.e., it is the *a priori* probability of an α-type jump; (cf. Ref. 9)]. We now recognize that $x_\alpha x_{\alpha,i}/a^2$ is ± 1 (ignoring as before jumps perpendicular to the x direction), and that $\langle x_\alpha x_{\alpha,i}/a^2 \rangle$ is equal to the probability that $x_{\alpha,i}$ is in the same direction as x_α minus the probability that it is in the opposite direction. Let us define the quantities $p_{j\pm}^{\alpha\beta}$ as equal to the probability that given an initial jump of type α, the jth jump following (excluding perpendicular jumps) is of type β with an x projection in the same $(+)$ or opposite $(-)$ direction as that of the initial jump.[16] Let

$$t_j^{\alpha\beta} = p_{j+}^{\alpha\beta} - p_{j-}^{\alpha\beta}. \tag{2.10}$$

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[16] It may happen that there are jumps of type α (as defined above), say α_k and α_l, for which $p_{j\pm}^{\alpha_l\beta} \neq p_{j\pm}^{\alpha_k\beta}$. Accordingly, we amend the definition of "type": Two jumps A and B with x projections x_A and x_B are of the same type if *both* of the following conditions are satisfied:

$$\Sigma_{i=1} \langle x_A x_{A,i} \rangle = \Sigma_{i=1} \langle x_B x_{B,i} \rangle, \tag{1}$$

and

$$p_{j\pm}^{A\beta} = p_{j\pm}^{B\beta}, \text{ (all types } \beta, \text{ all } j). \tag{2}$$

Here the subscripts A,i and B,i refer to the ith jumps following

Then

$$\langle x_\alpha x_{\alpha,i} \rangle / a^2 = \sum_{\beta=1}^{N} t_j^{\alpha\beta}. \tag{2.11}$$

It is now easy to show that the $t_j^{\alpha\beta}$ can be expressed in terms of $t_1^{\alpha\beta}$. We first note the following recursion relation for the $p_{j\pm}^{\alpha\beta}$:

$$p_{j+1\pm}^{\alpha\beta} = \sum_{\gamma=1}^{N} (p_{j+}^{\alpha\gamma} p_{1\pm}^{\gamma\beta} + p_{j-}^{\alpha\gamma} p_{1\mp}^{\gamma\beta}). \tag{2.12}$$

Hence,

$$t_{j+1}^{\alpha\beta} = \sum_{\gamma=1}^{N} t_j^{\alpha\gamma} t_1^{\gamma\beta}. \tag{2.13}$$

We may now construct the $N \times N$ matrix $\mathbf{T}_j$ with the elements $t_j^{\alpha\beta}$. Then from Eq. (2.13)

$$\mathbf{T}_j = (\mathbf{T}_1)^j, \tag{2.14}$$

which is the desired relation. From Eqs. (2.9), (2.11) and (2.14) we may now write for the correlation factor

$$f_x = 1 + 2\mathbf{c} \cdot \mathbf{T}_1 (\mathbf{I} - \mathbf{T}_1)^{-1} \cdot \mathbf{1}, \tag{2.15}$$

where $\mathbf{c}$ is the row matrix $(c_1, c_2, \cdots, c_N)$, and $\mathbf{I}$ is the $N \times N$ unit matrix and $\mathbf{1}$ the N-component unit column matrix. We have made use of the identity

$$(\mathbf{I} - \mathbf{T}_1)^{-1} = \mathbf{I} + \sum_{j=1}^{\infty} (\mathbf{T}_1)^j.$$

The extension of Eq. (2.15) to the case where the x_α are of different lengths is straightforward. We find in the more general case the expression

$$f_x = 1 + 2\mathbf{b} \cdot \mathbf{T}_1 (\mathbf{I} - \mathbf{T}_1)^{-1} \cdot \mathbf{d}, \tag{2.16}$$

where

$$\mathbf{d} = \begin{pmatrix} |x_1| \\ |x_2| \\ \vdots \\ |x_N| \end{pmatrix},$$

and

$$\mathbf{b} = (\sum_{\alpha=1}^{N} c_\alpha x_\alpha^2)^{-1} (c_1|x_1|, c_2|x_2|, \cdots c_N|x_N|).$$

Equations (2.15) and (2.16) are the desired generalizations of Eq. (2.8). They express f_x in terms of correlations between only successive jumps.

Consider the special case $N = 2$ and suppose that the x projections of the two types of jumps are of the same length. Then, Eq. (2.15) becomes

$$f_x = c_1 f_{x1} + c_2 f_{x2}, \tag{2.17}$$

the particular jumps A and B, respectively. The quantities $p_{j\pm}^{A\beta}$ and $p_{j\pm}^{B\beta}$ are the probabilities that the jth jumps following the particular jumps A and B, respectively, are jumps of type β with x projections in the same $(+)$ or in the opposite $(-)$ directions as those of the A and B jumps. We do not require that the classification into types be unique. In general, to make classifications into types may not be easy. However, for the cases we shall consider here, how to classify jumps will be obvious.

where

$$f_{x1}=\frac{(1+t^{11})(1-t^{22})+t^{12}(2+t^{21})}{(1-t^{11})(1-t^{22})-t^{12}t^{21}},\qquad(2.18)$$

and

$$f_{x2}=\frac{(1+t^{22})(1-t^{11})+t^{21}(2+t^{12})}{(1-t^{11})(1-t^{22})-t^{12}t^{21}}.\qquad(2.19)$$

(We here and henceforth drop the subscript 1 on the t^{ij}.) If, in addition, $c_1=c_2=\frac{1}{2}$, then

$$f_x=\frac{(1+t^{21})(1+t^{12})-t^{11}t^{22}}{(1-t^{11})(1-t^{22})-t^{12}t^{21}}.\qquad(2.20)$$

3. TRACER DIFFUSION BY PAIRS

A. Method of Calculation

We shall now apply the general results derived in the preceding section to calculate the correlation factor for cases of tracer diffusion by divacancy and impurity-vacancy pairs in cubic crystals. In cubic crystals, the correlation factor is isotropic; hence we need only calculate the correlation factor with respect to any one of the principle axes. The procedure of each of the calculations is as follows: We first classify the types of jumps that may occur and find the a priori probabilities of each type. This will give a relation between f_x and the $t^{\alpha\beta}$ via Eq. (2.15). We shall then calculate the $t^{\alpha\beta}$ by methods used by Bardeen and Herring[1] and by Mullen.[9] Here we shall suppose that initially the tracer makes a jump of a particular type into the origin; we shall specify the type of jump which has occurred by specifying the position, immediately after the tracer jump, of the pair which caused it. The diffusion of this pair is then followed until it again causes the tracer to move in the x direction. In this way we shall find the probability that the second tracer jump is of a particular type and that its x displacement is in a particular direction. This will yield the $t^{\alpha\beta}$ for all α and β.

An exact calculation of the $t^{\alpha\beta}$ involves following the wandering of the pair over all the sites in the crystal that are available to it. In practice, some approximation must be made which limits the number of pair sites. Following Mullen,[9] we shall in each case define a boundary surrounding the origin and suppose that if a pair wanders outside this boundary, it will return to the origin only randomly, and thus make no contribution to the $t^{\alpha\beta}$. Formally, this is equivalent to setting the occupation probabilities of pair sites outside the boundaries equal to zero for all times. Once such a boundary is chosen, the $t^{\alpha\beta}$ will be calculated with no further approximations.

In the cases we shall consider, it will always be possible on the basis of symmetry arguments to classify the pair sites within the chosen boundary into sets such that all pair sites within a given set have the same probability of being occupied. The number of pair sites that need to be considered explicitly may thus be limited to one from each set. Suppose that in a given case there are M such sets and that we have chosen M distinct pair sites. Suppose that we have ordered these in some definite way. Let $p_n(i)$ be the probability that the pair site $i(i=1, 2\cdots M)$ is occupied on the nth jump of the pair following the tracer jump, given that a second tracer jump (having nonzero x displacement) has not occurred. We construct the M-component column vector

$$\mathbf{p}_n=\begin{bmatrix}p_n(1)\\\vdots\\p_n(M)\end{bmatrix},\qquad(3.1)$$

which specifies the occupation-probability distribution after the nth jump. The vector $\mathbf{p}_0$ gives the distribution of occupied pair sites immediately after the tracer jump and thus specifies the type of jump which has occurred. It is clear that $\mathbf{p}_n$ is linearly related to $\mathbf{p}_{n-1}$ and we define an $M\times M$ matrix $\mathbf{A}$ such that

$$\mathbf{p}_n=\mathbf{A}\mathbf{p}_{n-1}.\qquad(3.2)$$

A typical matrix element A_{ij} is the probability that the particular site i is occupied after n pair jumps, given unit occupation probabilities after the $n-1$ jump for all pair sites in the set containing j. The elements of $\mathbf{A}$ will be found by inspection, in each particular case, in terms of relevent jump frequencies. We define the vector $\mathbf{P}$ by the equation

$$\mathbf{P}=\sum_{n=0}^{\infty}\mathbf{p}_n.\qquad(3.3)$$

The components of this vector give the probabilities that each of the sites i are occupied at some time during the interval between consecutive tracer jumps (excluding jumps perpendicular to the x direction). Substituting from Eq. (3.2), $\mathbf{P}$ may be expressed as follows:

$$\mathbf{P}=(\sum_{n=0}^{\infty}\mathbf{A}^n)\mathbf{p}_0=\boldsymbol{\beta}\cdot\mathbf{P}_0,\qquad(3.4)$$

where

$$\boldsymbol{\beta}\equiv(\mathbf{I}-\mathbf{A})^{-1}.\qquad(3.5)$$

Hence, $\mathbf{P}$ can be found if $\mathbf{p}_0$ and $\mathbf{A}$ are known. It will be clear in each of the particular cases that we shall save much effort if we choose initial probability distributions of occupied pair sites to be antisymmetric with respect to reflection in the yz plane. It is easy to show from symmetry arguments that the probability distribution remains antisymmetric for all n. It then follows that the occupation probabilities of corresponding groups of sites on either side of the yz plane differ only in sign. We shall need therefore to consider explicitly only typical members of groups having positive x coordinates. In addition, it will be possible to compute the $t^{\alpha\beta}$ directly from equations of the form

$$t^{\alpha\beta}=\mathbf{Q}^{(\beta)}\cdot\mathbf{P}^{(\alpha)}.\qquad(3.6)$$
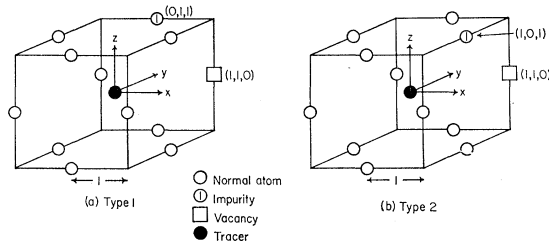
FIG. 1. Tracer jumps by bound impurity-vacancy pairs in an fcc lattice: (a) shows one of the sixteen possible configurations immediately after the type-1 tracer jump into the origin; (b) shows one of the sixteen possible configurations following a type-2 jump. Unit distance is taken as half the cube edge.

Here the superscript α denotes that $\mathbf{P}^{(\alpha)}$ is derived from an initial probability distribution appropriate to an α-type jump. The components $Q_i^{(\beta)}$ of the row vector $\mathbf{Q}^{(\beta)}$ are transition probabilities of pair jumps from groups of sites equivalent to i causing a β-type jump of the tracer. The $Q_i^{(\beta)}$, like the A_{ij} will be found by inspection in each case.

To summarize, we shall first obtain a relation between f_x and the $t^{\alpha\beta}$ by classifying the types of tracer jumps and by finding their *a priori* probabilities. Immediately after an α-type jump has occurred, one of a certain set of equivalent sites must be occupied by a pair. We shall choose certain (antisymmetric) superpositions of initial occupation probabilities to describe each α. A boundary will be defined outside of which the pair-site occupation probabilities are put equal to zero. (This is the only approximation in computing the $t^{\alpha\beta}$; the accuracy of the calculation may be increased by increasing the size of the boundary.) Sets of equivalent pair sites within the boundary will be distinguished and representative sites will be selected and ordered. The matrix $\mathbf{A}$ and the vector $\mathbf{Q}^{(\beta)}$ will be found by inspection in terms of vacancy jump frequencies and the $t^{\alpha\beta}$ calculated via Eqs. (3.4)–(3.6).

B. Impurity-Vacancy Pairs in NaCl-Type Ionic Crystals and in fcc Metals

Consider the diffusion of a tracer in one of the sublattices of a NaCl-type ionic crystal (or in an fcc metal) by exchanges with an impurity-vacancy pair which moves in the same sublattice. We may distinguish two types of tracer x displacements (see Fig. 1). Type 1 is from pairs for which the impurity has an x coordinate different from the initial position of the tracer (i.e., its position before its jump into the origin); type 2 from pairs for which the impurity has the same x coordinate. These two types of tracer jumps occur with the same *a priori* probability. Therefore, Eq. (2.20) applies. We label pair sites by listing the coordinates of the vacancy first, and then those of the impurity. Thus $p_n[\mathbf{v},\mathbf{i}]$ is the probability that the pair site $[\mathbf{v},\mathbf{i}]$ is occupied after the nth jump of the pair.

Let us suppose that the tracer has made a jump into a site which we shall take as the origin. In specifying site coordinates, we take as unit distance the distance between neighboring $\langle 100 \rangle$ planes. If the tracer jump is of type 1, then immediately after the jump one of the following sixteen pair sites must be occupied (see Fig. 1): $[(\pm 1, \pm 1, 0)(0, \pm 1, 1)]$, $[(\pm 1, 0, \pm 1) \times (0, 1, \pm 1)]$, $[(\pm 1, \pm 1, 0)(0, \pm 1, -1)]$, $[(\pm 1, 0, \pm 1) \times 0, -1, \pm 1)]$, where the signs of the y and also of the z coordinates of the impurity and vacancy are the same for each pair site. Similarly, one of the following sixteen sites must be occupied immediately after a type-2 jump: $[(\pm 1, 0, \pm 1)(\pm 1, 1, 0)]$, $[(\pm 1, 0, \pm 1)(\pm 1, -1, 0)]$, $[(\pm 1, \pm 1, 0)(\pm 1, 0, 1)]$, $[(\pm 1, \pm 1, 0)(\pm 1, 0, -1)]$, where now the x coordinates as well as the y and z coordinates of the impurity and vacancy are of the same sign. To take most advantage of the crystal symmetry we choose the following antisymmetric distributions to represent an initial type-1 and type-2 jump, respectively:

$$p_0^{(1)}[(1, \pm 1, 0)(0, \pm 1, 0)] = \text{etc.} = \tfrac{1}{8},$$
$$p_0^{(1)}[(-1 \pm 1, 0)(0, \pm 1, 0)] = \text{etc.} = -\tfrac{1}{8}, \tag{3.7}$$

and

$$p_0^{(2)}[(1, 0, \pm 1)(1, 1, 0)] = \text{etc.} = \tfrac{1}{8},$$
$$p_0^{(2)}[(-1, 0, \pm 1)(1, 1, 0)] = \text{etc.} = -\tfrac{1}{8}. \tag{3.8}$$

Such antisymmetric initial distributions allow the $t^{\alpha\beta}$ (rather than the $p_{\pm}^{\alpha\beta}$) to be calculated directly.

The symmetry of the distributions (3.7) and (3.8) together with the lattice symmetry imply that the occupation probabilities are the same of any two pair sites which can be obtained from each other by changing the sign of the y or of the z coordinates or by interchanging the y and z coordinates (these operations being applied to both members of the pair). Also, pair sites which can be obtained from each other by changing the sign of the x coordinates of both members have occupation probabilities which differ only in sign.

We now limit the number of pair sites which may have nonzero occupation probability to those for which at least one member neighbors on the origin. From the symmetry considerations of the preceding paragraph we find that there are 15 independent groups of pair sites having positive x coordinates. We list representative members of each group; the number of members of each group is given after each representative site:

(1) $[(1, 1, 0)(0, 1, 1)] 8$ (9) $[(0, 1, 1)(1, 1, 0)] 8$

(2) $[(1, 1, 0)(1, 0, 1)] 8$ (10) $[(2, 0, 0)(1, 1, 0)] 4$

(3) $[(1, 1, 0)(2, 0, 0)] 4$ (11) $[(0, 2, 0)(1, 1, 0)] 4$

(4) $[(1, 1, 0)(0, 2, 0)] 4$ (12) $[(2, 2, 0)(1, 1, 0)] 4$

(5) $[(1, 1, 0)(2, 2, 0)] 4$ (13) $[(2, 1, 1)(1, 1, 0)] 8$

(6) $[(1, 1, 0)(2, 1, 1)] 8$ (14) $[(1, 2, 1)(1, 1, 0)] 8$

(7) $[(1, 1, 0)(1, 2, 1)] 8$ (15) $[(1, 2, 1)(0, 1, 1)] 8.$

(8) $[(0, 1, 1)(1, 2, 1)] 8$

We have not listed pair sites both of whose members have zero x coordinates since, from symmetry, the occupation probability of these is always zero. The initial probability-distribution vectors may now be written as the 15-component column vectors

$$\mathbf{p}_0^{(1)} = \begin{bmatrix} 1/8 \\ 0 \\ 0 \\ \vdots \\ 0 \end{bmatrix}, \qquad \mathbf{p}_0^{(2)} = \begin{bmatrix} 0 \\ 1/8 \\ 0 \\ 0 \\ \vdots \\ 0 \end{bmatrix}. \tag{3.9}$$

The elements A_{ij} of the matrix $\mathbf{A}$ are the transition probabilities of pair jumps out of the group of sites equivalent to j into the single site i. We find by inspection

$$\mathbf{A} = \begin{bmatrix}
a & 0 & 0 & 0 & 0 & 0 & 0 & 0 & b & 0 & 0 & 0 & 0 & 0 & a \\
0 & b & 0 & 0 & 0 & 0 & 0 & 0 & a & a & 0 & 0 & a & 0 & 0 \\
0 & 0 & 2a & 0 & 0 & 0 & 0 & 0 & 0 & b & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & b & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & b & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & a & 0 & 0 & 0 & 0 & 0 & 0 & b & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & a & 0 & 0 & 0 & 0 & 0 & b & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & a & 0 & 0 & 0 & 0 & 0 & 0 & 0 & b \\
b & a & 0 & 0 & 0 & 0 & 0 & 0 & a & 0 & a & 0 & 0 & a & 0 \\
0 & 2a & b & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 2a & 0 & 0 \\
0 & 0 & 0 & b & 0 & 0 & 0 & 0 & 2a & 0 & 0 & 0 & 0 & 2a & 0 \\
0 & 0 & 0 & 0 & b & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 2a & 2a & 0 \\
0 & a & 0 & 0 & 0 & b & 0 & 0 & 0 & a & 0 & a & 0 & a & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & b & 0 & a & 0 & a & a & a & 0 & 0 \\
a & 0 & 0 & 0 & 0 & 0 & 0 & b & 0 & 0 & 0 & 0 & 0 & 0 & a
\end{bmatrix}.$$

Here,

$$a = 1/(4+\delta),$$

and

$$b = \delta/(4+\delta),$$

where $\delta = \nu_2/\nu_1$ is the ratio of the exchange frequencies of a vacancy with the impurity (ν_2) and with one of the normal atoms surrounding the impurity (ν_1). The vectors $\mathbf{Q}^{(\alpha)}$ are found by inspection to be

$$\mathbf{Q}^{(1)} = -8a(0, 1, 0, 0\cdots0),$$
$$\mathbf{Q}^{(2)} = -8a(1, 0, 0\cdots0). \tag{3.10}$$

The $t^{\alpha\beta}$ may now be computed from Eq. (3.4)–(3.6). We find explicitly $t^{11} = -a\beta_{21}$, $t^{21} = -a\beta_{22}$, $t^{12} = -a\beta_{11}$, $t^{22} = -a\beta_{12}$. Substituting into Eq. (2.20) gives

$$f = \frac{1 - a(\beta_{11}+\beta_{22}) + a^2(\beta_{11}\beta_{22}-\beta_{12}\beta_{21})}{(1+a\beta_{21})(1+a\beta_{12}) - a^2\beta_{11}\beta_{22}}. \tag{3.11}$$

The values of β_{11}, etc. are found by inverting the matrix $(\mathbf{I}-\mathbf{A})$ for selected values of δ. Values of f versus δ are listed in Table I along with the more accurate (but widely spaced) values obtained by Compaan and Haven (C-H) from analog computer calculations. A comparison shows that the present calculation gives values of the correlation factor that are larger than the C-H values by 5 to 6%. The accuracy could be improved by choosing a more extensive boundary and such an improvement could be carried out without excessive trouble.

It is to be expected, of course, that the present method of obtaining the $t^{\alpha\beta}$ will always overestimate f (i.e., underestimate correlation effects). The present calculations are in agreement with those of Reiss[17] done

TABLE I. Correlation factors for tracer diffusion by bound impurity-vacancy pairs in an fcc lattice. The quantity δ is the ratio of the exchange frequency of a vacancy with an impurity to that of a vacancy with a normal ion; ν_1' is the exchange frequency of a vacancy with the tracer. The values of f were calculated assuming the transmitting boundary described in the text, and those of f(refl.) assuming a reflecting boundary. The values f(C−H) were taken from Ref. 6.

δ	f	$1+\dfrac{d\ln f}{d\ln\nu_1'}$	f(C−H)	f(refl.)	δ	f	f(C−H)	f(refl.)
0.0010	0.0044	0.012		0.0019	7.0	0.49		
0.0021	0.0094	0.017			10.0	0.50	0.4711	0.32
0.0031	0.0134	0.021			100	0.51		0.32
0.0042	0.018	0.025			∞		0.4862	0.32
0.0051	0.021	0.029						
0.0061	0.026	0.033						
0.0081	0.034	0.040						
0.011	0.044	0.050		0.019				
0.031	0.10	0.11						
0.050	0.15	0.15						
0.080	0.20	0.20						
0.1			0.2047	0.12				
0.11	0.23							
0.21	0.30							
0.30	0.33							
0.40	0.36							
0.50	0.37		0.3540					
0.60	0.39							
0.80	0.41							
1.0	0.42		0.3977	0.27				
1.5	0.44							
2.0	0.45							
3.0	0.47							
5.0	0.48							

[17] H. Reiss, Phys. Rev. 113, 1445 (1959).

by a different method but involving essentially the same approximations. The values of the correlation factor designated as f(refl.) were calculated by the methods described above but assuming a boundary which stops pairs from moving so far from the tracer that neither of its members neighbor on it. Such a reflecting boundary overestimates correlation effects and therefore gives lower limits to the correlation factor. We note that the Compaan and Haven values lie between the values of f and f(refl.) but much closer to the values of f. As might be expected, the transmitting boundary is the better approximation.[18]

C. Isotope Effect: Impurity-Vacancy Pairs

We have assumed in Sec. 3B that the exchange frequencies of a vacancy with tracer and with normal host atoms are the same. However, the tracer and the normal host atoms may have different masses and, because of this, somewhat different jump frequencies. It is sometimes possible to take advantage of such a difference to study the correlation factor directly by studying the simultaneous diffusion in the same host crystal of two different isotopes of the same tracer.[12,19,20]

Consider the *difference* between the diffusion coefficient of two isotopes labeled a and b. In an obvious notation we write

$$\begin{aligned} D_a &= cf_a\nu_{1a}' , \\ D_b &= cf_b\nu_{1b}' , \end{aligned} \qquad (3.12)$$

where the constant c is the same for the two species and where we use a prime to denote the frequency of vacancy-tracer (as opposed to a vacancy-normal atom) exchange. Then

$$\frac{D_a-D_b}{D_a}=\frac{f_a\nu_{1a}'-f_b\nu_{1b}'}{f_a\nu_{1a}'}=-\left(1+\frac{\partial \ln f}{\partial \ln\nu_1'}\right)\left(\frac{\partial \ln\nu_1'}{\partial m}\right)\delta m \tag{3.13}$$

to first order in $\delta m = m_b - m_a$. Assume that $\nu_{1a,b}\propto(1/m_{a,b})^{1/2}$. [Vineyard[21] has discussed the physical basis of this assumption; it appears to be valid for self diffusion in Pd (Ref. 22) and for cation self-diffusion in NaCl (Ref. 12) but may not be for self-diffusion in Na metal[23].] Then Eq. (3.13) becomes[19,20]

$$(D_a-D_b)/D_a=(1+(\partial \ln f/\partial \ln\nu_1'))\delta m/2m . \tag{3.14}$$

(See Ref. 24.) For diffusion by a single-vacancy mecha-

[18] cf. A. D. Franklin, J. Res. Nat. Bur. Std. **69A**, 301 (1965).
[19] A. H. Schoen, Phys. Rev. Letters **1**, 524 (1958).
[20] A. B. Lidiard, *Proceedings of the Fourth International Symposium on Reactivity of Solids, Amsterdam* (Elsevier, Amsterdam, 1960), p. 52.
[21] G. H. Vineyard, J. Phys. Chem. Solids **3**, 121 (1957).
[22] N. L. Peterson, Phys. Rev. **136**, A568 (1964).
[23] L. H. Barr and J. N. Mundy, *Diffusion in Body-Centered Cubic Metals* (American Society for Metals, 1965), p. 171.
[24] We note that Eq. (21) in Ref. 12 is wrong because the differentiation is carried out with respect to ν_1 instead of ν_1'. Hence those results of Ref. 12 which are based on Eq. (21) are wrong.

nism in cubic crystals f is of the form[19,20]

$$f=A/(A+\nu_1') , \tag{3.15}$$

where A is dependent of ν_1'. In this case

$$1+(\partial \ln f/\partial \ln\nu_1')=f, \tag{3.16}$$

and hence

$$(D_a-D_b)/D_a=f(\delta m/2m) . \tag{3.17}$$

Under the conditions where this equation is valid, f can be measured directly.

For diffusion by an impurity-vacancy pair mechanism, it is not clear over what range of jump frequency ratios and to what approximation Eq. (3.16) is satisfied. We therefore wish to calculate the expression $1+(\partial \ln f/\partial \ln\nu_1')$. The calculation of $f(\nu_1')$ is carried out by simply replacing ν_1 by ν_1' in the equations of the preceding section whenever a tracer rather than a normal ion exchange is involved. It is easily checked that Eq. (3.11) is replaced by the equation

$$f(\nu_1')=\frac{1-a'(\beta_{11}'+\beta_{22}')+a'^2(\beta_{11}'\beta_{22}'-\beta_{12}'\beta_{21}')}{(1+a'\beta_{21}')(1+a'\beta_{12}')-a'^2(\beta_{11}'\beta_{22}')}, \tag{3.18}$$

where

$$a'=\nu_1'/(\nu_2+3\nu_1+\nu_1') . \tag{3.19}$$

The β_{ij}' are elements of the matrix $(I-A')^{-1}$ where the matrix A' is identical to the matrix A except for the following replacements:

$A_{99} \rightarrow a'$,	$A_{22} \rightarrow b'$,	$A_{19} \rightarrow b'$,
$A_{11} \rightarrow a''$,	$A_{92} \rightarrow a''$,	$A_{29} \rightarrow a'$,
$A_{91} \rightarrow b'$,	$A_{10,2} \rightarrow 2a''$,	$A_{11,9} \rightarrow 2a'$,
$A_{15,1} \rightarrow a''$,	$A_{13,2} \rightarrow a''$,	$A_{14,9} \rightarrow a'$.

Here,

$$a''=\nu_1/(\nu_2+3\nu_1+\nu_1') , \tag{3.20}$$

and

$$b'=\nu_2/(\nu_2+3\nu_1+\nu_1') . \tag{3.21}$$

The elements of A which remain unchanged do not involve vacancy-tracer interchanges.

Table I lists values of $1+(\partial \ln f/\partial \ln\nu_1')$ as a function of $\delta=\nu_2/\nu_1$. It is apparent that the relative difference between this quantity and the corresponding value of f is appreciable only for small δ, becoming less than 5% (the accuracy of the present calculation of f), for $\delta>0.1$.

D. Divacancy Pairs in NaCl-Type Ionic Crystals

To be definite, we suppose that the tracers are cations. We may again distinguish two types of tracer jumps according to whether the anion vacancy has an x coordinate (1) different from or (2) the same as the tracer before its jump (see Fig. 2). The *a priori* probabilities of these kinds of jumps are the same and hence Eq. (2.20) applies. We label divacancy pair sites by specifying the midpoints of the line joining the indi-

vidual vacancy sites and define $p_n(x,y,z)$ as equal to the probability that the nth cation vacancy jump (following the initial displacement of the tracer) fills the pair site (x,y,z) (given that a second tracer displacement in the x direction has not yet occurred). We again assume that the initial tracer jump is into the origin and choose the following initial probability distributions to represent a type (1) jump and a type (2) jump, respectively:

$$p_0^{(1)}(\tfrac{1}{2}, \pm 1, 0) = p_0^{(1)}(\tfrac{1}{2}, 0, \pm 1) = \tfrac{1}{4},$$
$$p_0^{(1)}(-\tfrac{1}{2}, \pm 1, 0) = p_0^{(1)}(-\tfrac{1}{2}, 0, \pm 1) = -\tfrac{1}{4},$$ (3.22)

and

$$p_0^{(2)}(1, \pm\tfrac{1}{2}, 0) = p_0^{(2)}(1,0, \pm\tfrac{1}{2}) = \tfrac{1}{4},$$
$$p_0^{(2)}(-1, \pm\tfrac{1}{2}, 0) = p_0^{(2)}(-1, 0, \pm\tfrac{1}{2}) = -\tfrac{1}{4}.$$ (3.23)

Here, we have taken the anion-cation distance as unity. Our choice of initial occupation probabilities implies that

$$p_n(x,y,z) = -p_n(-x, y, z)$$
$$= p_n(x, \pm y, \pm z) = p_n(x, \pm z, \pm y).$$ (3.24)

In particular

$$p_n(0,y,z) \equiv 0.$$ (3.25)

Equation (3.24) may be used as a basis for choosing groups of equivalent pair sites.

We again restrict the number of pair sites having nonzero occupation probability to those for which at least one member neighbors on the tracer at the origin. We find that there are seven independent groups of such pair sites. Representative members and multiplicities of each group may be ordered as follows:

(1) $(\tfrac{1}{2},1,0)$ 4   (4) $(1,1,\tfrac{1}{2})$ 8

(2) $(1,\tfrac{1}{2},0)$ 4   (5) $(\tfrac{1}{2},1,1)$ 8

(3) $(\tfrac{3}{2},0,0)$ 1   (6) $(\tfrac{3}{2},1,0)$ 4

(7) $(1,\tfrac{3}{2},0)$ 4.

We then have for the initial occupation probability vectors

$$\mathbf{p}_0^{(1)} = \begin{bmatrix} \tfrac{1}{4} \\ 0 \\ 0 \\ 0 \\ \vdots \\ 0 \end{bmatrix}, \qquad \mathbf{p}_0^{(2)} = \begin{bmatrix} 0 \\ \tfrac{1}{4} \\ 0 \\ 0 \\ \vdots \\ 0 \end{bmatrix}.$$ (3.26)

The reader will note that we have enumerated pair jumps by counting only those of the cation vacancy. The subscript n appearing in Eqs. (3.22)–(3.25) represents the number of cation vacancy jumps of the pair following the jump of the tracer. The anion vacancy jumps are taken into account by computing the probabilities of the pair reorientations that may occur between cation vacancy jumps.

We define certain reorientation probabilities as follows: Suppose that the pair occupies the site shown

FIG. 2. Cation tracer jumps by bound divacancy pairs in a NaCl-type ionic crystal: (a) shows one of the eight possible configurations immediately after a type-1 tracer jump into the origin; (b) shows one of the sixteen possible configurations following a type-2 jump. The cation sites are at the midpoints of the cube edges; the cation tracer is at the center of the cube. The anion sites are at the corners of the cube and at the centers of the cube faces. The anion-cation separation is taken as unit distance.

in Fig. 3 with the anion vacancy at the site labeled (a). We define q_1, $4q_2$ and q_3 as the probabilities that upon the next cation vacancy jump, the anion vacancy is at the site (a), one of the sites (b–e) and the site (f), respectively (i.e., the sites that can be reached from the original anion vacancy site by a minimum of zero, one or two anion vacancy jumps, respectively). Clearly, $q_1 + q_2 + 4q_3 = 1$. By inspection, we find the following matrix for $\mathbf{A}$ in terms of the q_i:

$$\mathbf{A} = \frac{1}{4} \begin{bmatrix} 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 2q_3 & 2q_1 & q_1 & 4q_3 & 0 & 2q_3 & 2q_2 \\ 4q_1 & 4q_3 & 0 & 8q_3 & 0 & 4q_3 & 4q_2 \\ q_3 & q_3 & 0 & q_1+q_2 & q_1-q_2 & q_3 & q_3 \\ 2q_3 & 2q_3 & 0 & 2(q_1+q_2) & 0 & 2q_3 & 2q_3 \\ 0 & 0 & q_3 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix}.$$ (3.27)

The vectors $\mathbf{Q}^{(1,2)}$ are given by the expressions

$$\mathbf{Q}^{(1)} = -(q_3,q_1,0,2q_3,0,q_2,q_3),$$
$$\mathbf{Q}^{(2)} = -(q_1,q_3,0,2q_3,0,q_3,q_2).$$ (3.28)

Explicit expressions for the q_i as a function of $\delta = \nu_2/\nu_1$, the ratio of the anion-vacancy jump frequency to that of the cation vacancy, are given in the Appendix. Values of f versus δ computed from Eqs. (3.4)–(3.6) and (2.20) are listed in Table II along with values from Compaan and Haven.[6] The values of f computed here are larger than those of Compaan and Haven by about 3% over the entire range of δ.

E. Divacancy Pairs in CsCl-Type Ionic Crystals

Here there is only a single type of vacancy jump (see Fig. 4). Hence Eq. (2.17) for the correlation factor

FIG. 3. The six nearest-neighbor anion sites of the cation vacancy $\boxed{C}$ in a NaCl-type ionic crystal. These are at the center of the faces of the cube surrounding $\boxed{C}$. Initially, an anion vacancy is at the site (a).
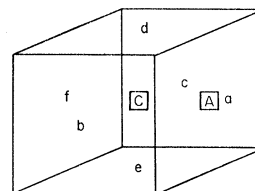
TABLE II. Correlation factors for cation tracer diffusion by bound divacancy pairs in a NaCl-type ionic crystal. The quantity δ is the ratio of the jump frequency of the anion vacancy to that of the cation vacancy. The values $f(C-H)$ are taken from Ref. 6.

δ	f	$f(C-H)$	δ	f	$f(C-H)$
0.001	0.0050		3.0	0.73	
0.002	0.0098		4.17		0.7451
0.003	0.0146		5.0	0.76	
0.004	0.0194		7.0	0.78	0.7793
0.005	0.024		10.0	0.79	
0.006	0.029		100	0.81	
0.007	0.033		1000	0.82	0.7815
0.008	0.038		∞		
0.009	0.042				
0.01	0.046				
0.03	0.12				
0.05	0.18				
0.07	0.23				
0.09	0.27				
0.10	0.28				
0.20	0.40				
0.24		0.4136			
0.3	0.47				
0.4	0.51				
0.5	0.54	0.5283			
0.7	0.59				
0.9	0.62				
1.0	0.63	0.6189			
1.5	0.68				
2.0	0.70	0.6894			

reduces to the expression

$$f = (1 + t^{11})/(1 - t^{11}) . \qquad (3.29)$$

Again we consider the diffusion of a cation tracer and take as the initial probability distribution

$$p_0(3, \pm 1, \pm 1) = \tfrac{1}{4},$$
$$p_0(-3, \pm 1, \pm 1) = -\tfrac{1}{4}, \qquad (3.30)$$

where the sites are labeled by the midpoint of the line joining the two vacant sites; the tracer is at the origin. We have taken the unit distance as $\tfrac{1}{4}$ the separation of nearest-neighbor cation sites. It is clear from symmetry that Eq. (3.24) again applies. As in the preceding sections, we limit the pair sites with nonzero occupation probability to those having at least one member neighboring on the tracer. There are seven such groups of
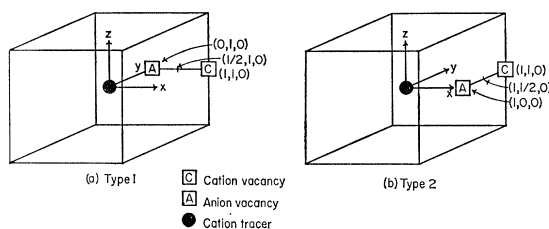

FIG. 4. Cation tracer jump by bound divacancy pairs in a CsCl-type ionic crystal. The figure shows one of the eight possible configurations immediately after a tracer jump into the origin. The unit distance is taken as $4\times$ the anion-cation separation.

sites. We list representative members and multiplicities of each group as follows:

1. (3,1,1) 4   4. (1,5,1) 8
2. (5,1,1) 4   5. (1,3,3) 4
3. (1,3,1) 8   6. (3,3,1) 8
                    7. (3,3,3) 4.

The vector $\mathbf{p}_0$ giving the initial probability distribution is then

$$\mathbf{p}_0 = \begin{pmatrix} \tfrac{1}{4} \\ 0 \\ 0 \\ 0 \\ \vdots \\ 0 \end{pmatrix} . \qquad (3.31)$$

We again enumerate successive cation-vacancy jumps and calculate reorientations due to anion-vacancy jumps by introducing the reorientation probabilities q_i, $(i=1,\cdots 4)$: Given that a vacancy pair is situated as shown in Fig. 5, q_1, $3q_2$, $3q_3$, and q_4 are the probabilities that when the next cation vacancy jump occurs, the anion vacancy occupies the site (a), one of the three sites (b–d), one of the three sites (e–g), or the site (h), respectively (i.e., sites that can be reached from site (a) by a minimum of zero, one, two, or three anion vacancy jumps, respectively). The calculation of these quantities as a function of δ, the ratio of anion vacancy to cation-vacancy jump frequencies, is given in Appendix B. In terms of these probabilities we find for the matrix $\mathbf{A}$:

$$\mathbf{A} = \frac{1}{3} \begin{bmatrix} 0 & 0 & 0 & 0 & 0 & 2(q_1+q_2) & 0 \\ 0 & 0 & 0 & 0 & 0 & 2(q_2+q_3) & 0 \\ 0 & 0 & q_1-q_3 & q_2-q_4 & q_1-q_2 & q_1+q_2 & 0 \\ 0 & 0 & 0 & 0 & q_2-q_3 & q_2+q_3 & 0 \\ 0 & 0 & 2(q_1-q_3) & 2(q_2-q_4) & 0 & 0 & q_1 \\ q_1+2q_2+q_3 & q_2+2q_3+q_4 & q_1-q_3 & q_2-q_4 & 0 & 0 & q_1 \\ 0 & 0 & 0 & 0 & q_1-q_2 & q_1+q_2 & 0 \end{bmatrix} , \qquad (3.32)$$

and for the vector $\mathbf{Q}$,

$$\mathbf{Q} = -\tfrac{4}{3}[(q_1+2q_2+q_3) , (q_2+2q_3+q_4) , 0,0,0,0,0] . \qquad (3.33)$$

Table III gives values of f versus δ. As $\delta \to \infty$, the corre-

lation factor must approach that for tracer diffusion by single vacancies in a simple cubic crystal. This is 0.66 as computed by Compaan and Haven.[6] We find $f=0.70$ for $\delta=3200$, about 5% too large. We estimate that this is the error in f over the entire range of δ.

F. Divacancies in an fcc Metal

Here the two vacancies in the pair are equivalent; hence the correlation factor is a number independent of jump frequencies. We distinguish two types of jumps: those caused by pairs both of whose vacancies have different x coordinates from the tracer (type 1) and by pairs which have one vacancy with the same x coordinate as the initial tracer position (type 2) (see Fig. 6). These types occur with the same *a priori* probability; hence Eq. (2.20) applies. The two distributions describing initial jumps of type (1) and (2) are:

$$p_0^{(1)}(\tfrac{1}{2}, \pm 1, \pm \tfrac{1}{2}) = p_0^{(1)}(\tfrac{1}{2}, \pm \tfrac{1}{2}, \pm 1) = \tfrac{1}{8},$$
$$p_0^{(1)}(-\tfrac{1}{2}, \pm 1, \pm \tfrac{1}{2}) = p_0^{(1)}(-\tfrac{1}{2}, \pm \tfrac{1}{2}, \pm 1) = -\tfrac{1}{8}, \qquad (3.34)$$

and

$$p_0^{(2)}(1, \pm \tfrac{1}{2}, \pm \tfrac{1}{2}) = \tfrac{1}{4},$$
$$p_0^{(2)}(-1, \pm \tfrac{1}{2}, \pm \tfrac{1}{2}) = -\tfrac{1}{4}. \qquad (3.35)$$

We have labeled the pair sites by the midpoint joining the site of the individual pairs, with the origin at the tracer and the lattice spacing along a cube direction as unit distance. The symmetry conditions given by Eq. (3.24) apply. We choose a more extended boundary than heretofore and allow those pair sites to have nonzero occupation probability for which (at least) one member is a nearest neighbor or a next-nearest neighbor of the tracer. This gives 27 independent groups of pair sites. Representative sites and multi-

FIG. 5. The eight nearest-neighbor anion sites of the cation vacancy Ⓒ in a CsCl-type ionic crystal. These are at the corners of a cube surrounding Ⓒ. Initially an anion vacancy is at the site (a).

plicities are listed as follows:

1. $(\tfrac{1}{2}, 1, \tfrac{1}{2})$ 8	10. $(\tfrac{1}{2}, 2, \tfrac{3}{2})$ 8	19. $(\tfrac{3}{2}, \tfrac{5}{2}, 0)$ 4
2. $(1, \tfrac{1}{2}, \tfrac{1}{2})$ 4	11. $(\tfrac{1}{2}, \tfrac{5}{2}, 0)$ 4	20. $(\tfrac{3}{2}, \tfrac{5}{2}, 1)$ 8
3. $(\tfrac{3}{2}, \tfrac{1}{2}, 0)$ 4	12. $(\tfrac{1}{2}, \tfrac{5}{2}, 1)$ 8	21. $(2, \tfrac{1}{2}, \tfrac{1}{2})$ 4
4. $(\tfrac{1}{2}, \tfrac{3}{2}, 0)$ 4	13. $(1, \tfrac{3}{2}, \tfrac{3}{2})$ 4	22. $(2, \tfrac{3}{2}, \tfrac{1}{2})$ 8
5. $(\tfrac{3}{2}, \tfrac{3}{2}, 0)$ 4	14. $(1, \tfrac{5}{2}, \tfrac{1}{2})$ 8	23. $(2, \tfrac{3}{2}, \tfrac{3}{2})$ 4
6. $(\tfrac{3}{2}, 1, \tfrac{1}{2})$ 8	15. $(1, \tfrac{5}{2}, \tfrac{3}{2})$ 8	24. $(\tfrac{5}{2}, \tfrac{1}{2}, 0)$ 4
7. $(1, \tfrac{3}{2}, \tfrac{1}{2})$ 8	16. $(\tfrac{3}{2}, \tfrac{3}{2}, 1)$ 8	25. $(\tfrac{5}{2}, 1, \tfrac{1}{2})$ 8
8. $(\tfrac{1}{2}, \tfrac{3}{2}, 1)$ 8	17. $(\tfrac{3}{2}, 2, \tfrac{1}{2})$ 8	26. $(\tfrac{5}{2}, \tfrac{3}{2}, 0)$ 4
9. $(\tfrac{1}{2}, 2, \tfrac{1}{2})$ 8	18. $(\tfrac{3}{2}, 2, \tfrac{3}{2})$ 8	27. $(\tfrac{5}{2}, \tfrac{3}{2}, 1)$ 8.

The initial probability-distribution vectors are

$$\mathbf{p}_0^{(1)} = \begin{pmatrix} \tfrac{1}{8} \\ 0 \\ 0 \\ \vdots \\ 0 \end{pmatrix}, \qquad \mathbf{p}_0^{(2)} = \begin{pmatrix} 0 \\ \tfrac{1}{4} \\ 0 \\ 0 \\ \vdots \\ 0 \end{pmatrix}, \qquad (3.36)$$

and the matrix **A**:

$$\mathbf{A} = \frac{1}{8}\begin{bmatrix}
2 & 1 & 0 & 1 & 0 & 0 & 1 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
2 & 0 & 2 & 0 & 0 & 2 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 2 & 2 & 0 & 0 & 2 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 2 & 0 & 0 & 0 & 0 & 0 & 0 \\
2 & 0 & 0 & 0 & 0 & 0 & 2 & 0 & 2 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 2 & 2 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 2 & 0 & 0 & 0 & 2 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 1 & 1 & 0 & 1 & 1 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 1 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\
1 & 0 & 0 & 1 & 1 & 1 & 0 & 1 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
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0 & 0 & 2 & 0 & 0 & 2 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 2 & 2 & 0 & 0 \\
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0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 2 & 0 & 0 & 2 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 1 & 0 & 1 & 0 & 1
\end{bmatrix}. \qquad (3.37)$$
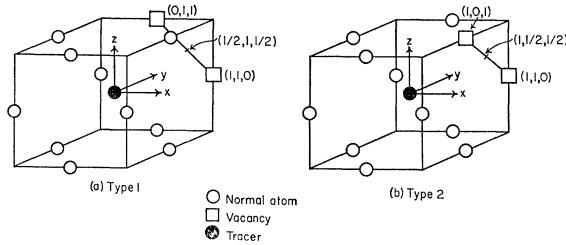
Fig. 6. Tracer jumps by bound divacancy pairs in a fcc crystal: (a) shows one of the sixteen possible configurations immediately following a type-1 jump of a tracer into the origin; (b) one of the eight possible configurations following a type-2 jump. The unit distance is taken as twice the cube edge.

The vectors $\mathbf{Q}$ are

$$\mathbf{Q}^{(1)} = -(0,1,0,0,\cdots),$$
$$\mathbf{Q}^{(2)} = -(1,0,0,\cdots). \qquad (3.38)$$

Substituting into Eqs. (3.4)–(3.6) gives

$$t^{11} = -\tfrac{1}{8}\beta_{21}, \qquad t^{12} = -\tfrac{1}{8}\beta_{11},$$
$$t^{21} = -\tfrac{1}{4}\beta_{22}, \qquad t^{22} = -\tfrac{1}{4}\beta_{12}.$$

The β_{ij} are found by inverting $(\mathbf{I}-\mathbf{A})$. After substituting into Eq. (2.22) we find $f=0.475$, a value slightly more than half that for tracer diffusion by single vacancies in an fcc lattice. In a previous calculation, Schottky[25] found the value $f=0.54$. To obtain this result, however, Schottky used Eq. (1.2) which is not valid in this case.

Table III. Correlation factors for cation tracer diffusion by bound divacancy pairs in a CsCl-type ionic crystal. The quantity δ is the ratio of the jump frequency of the anion vacancy to that of the cation vacancy.

δ	f	δ	f
0.0011	0.0094	3.2	0.61
0.0021	0.018	5.2	0.64
0.0031	0.026	7.6	0.65
0.0041	0.034	10.1	0.66
0.0049	0.040	25	0.68
0.0060	0.048	50	0.69
0.0079	0.062	100	0.695
0.011	0.078	3200	0.70
0.021	0.13		
0.030	0.17		
0.053	0.23		
0.086	0.29		
0.10	0.31		
0.20	0.38		
0.30	0.42		
0.39	0.44		
0.52	0.47		
0.64	0.49		
0.85	0.51		
1.0	0.53		
1.5	0.56		
2.0	0.58		

[25] G. Schottky, Phys. Letters 12, 95 (1964).

4. SUMMARY AND CONCLUSION

A method is presented whereby correlation factors can be calculated in situations where there is low symmetry by the same techniques that have been used in random-walk calculations of correlation factors for simple cases. The general method is used to calculate correlation factors for cases of tracer diffusion by bound impurity-vacancy and divacancy pairs in cubic metals and ionic crystals. The present calculations tend to overestimate correlation factors by about 5% in all cases where results can be compared with more accurate calculations. Such accuracy can be improved, if desired, by choosing larger boundaries within which correlation effects are included. The method can be applied without modification to the calculation of correlation factors for impurity diffusion as well as tracer diffusion. The case of tracer diffusion by impurity-vacancy pairs which may dissociate is also tractable and will be treated in a forthcoming paper.

APPENDIX: REORIENTATION PROBABILITIES FOR DIVACANCY PAIRS

Divacancies in NaCl-Type Ionic Crystals

We calculate here the reorientation probabilities q_i, $(i=1-3)$, defined in Sec. (3D). Referring to Fig. 3, the sites labeled $(a,b,\cdots f)$ are the six anion sites which neighbor on the cation-vacancy site as shown. Suppose that at the time $t=0$, the anion vacancy occupies the site (a). Let $w(a,t)$ equal the probability that the anion vacancy occupies the site (a) at the time t, given that the cation vacancy has not made a jump away from 0. The quantities $w(b,t)=w(c,t)=w(d,t)=w(e,t)$ and $w(f,t)$ are defined in the same way. The $w(a,t)$ etc. may be found by solving the following set of equations:

$$dw(a,t)/dt = 4\nu_2(w(b,t)-w(a,t)), \qquad (A1)$$
$$dw(b,t)/dt = \nu_2(w(a,t)+w(f,t)-2w(b,t)), \qquad (A2)$$
$$dw(f,t)/dt = 4\nu_2(w(b,t)-w(f,t)), \qquad (A3)$$

with the boundary conditions

$$w(a,0)=1; \quad w(b,0)=w(f,0)=0. \tag{A4}$$

The q_i then satisfy the equations

$$q_1=4\nu_1\int_0^\infty e^{-4\nu_1 t}w(a,t)dt, \tag{A5}$$

$$q_2=4\nu_1\int_0^\infty e^{-4\nu_1 t}w(f,t)dt, \tag{A6}$$

$$q_3=4\nu_1\int_0^\infty e^{-4\nu_1 t}w(b,t)dt. \tag{A7}$$

We find the following expressions for the q_i in terms of δ:

$$q_1=\tfrac{1}{6}\left(1+\frac{3}{1+\delta}+\frac{4}{2+3\delta}\right), \tag{A8}$$

$$q_2=\tfrac{1}{6}\left(1-\frac{3}{1+\delta}+\frac{4}{2+3\delta}\right), \tag{A9}$$

$$q_3=\tfrac{1}{6}\left(1-\frac{2}{2+3\delta}\right), \tag{A10}$$

where $\delta=\nu_2/\nu_1$.

Divacancies in CsCl-Type Ionic Crystals

Referring to Fig. 5, the sites labeled $(a\text{-}h)$ are the eight anion sites neighboring on the cation vacancy. The probabilities $w(a,t)$, $w(b,t)=w(c,t)$, $w(e,t)=w(f,t)=w(g,t)$, and $w(h,t)$ are defined as in (A1) and satisfy the equations

$$dw(a,t)/dt=3\nu_2(w(b,t)-w(a,t)), \tag{A11}$$

$$dw(b,t)/dt=\nu_2(w(a,t)-3w(b,t)+2w(e,t)), \tag{A12}$$

$$dw(e,t)/dt=\nu_2(2w(b,t)-3w(e,t)+w(h,t)), \tag{A13}$$

$$dw(h,t)/dt=3\nu_2(w(e,t)-w(h,t)), \tag{A14}$$

with the boundary conditions

$$w(a,0)=1; \quad w(b,0)=w(e,0)=w(h,0)=0. \tag{A15}$$

The q_i are defined as in Sec. 3E and are given in terms of the probabilities $w(a,t)$, etc. by the equations

$$q_1=3\nu_1\int_0^\infty e^{-3\nu_1 t}w(a,t)dt, \tag{A16}$$

$$q_2=3\nu_1\int_0^\infty e^{-3\nu_1 t}w(b,t)dt, \tag{A17}$$

$$q_3=3\nu_1\int_0^\infty e^{-3\nu_1 t}w(e,t)dt, \tag{A18}$$

$$q_4=3\nu_1\int_0^\infty e^{-3\nu_1 t}w(h,t)dt. \tag{A19}$$

Equations (A11)–(A19) yield the following expressions for the q_i:

$$q_1=\frac{3}{8}\left(\frac{1}{3}+\frac{3}{3+2\delta}+\frac{3}{3+4\delta}+\frac{1}{3(1+2\delta)}\right), \tag{A20}$$

$$q_2=\frac{3}{8}\left(\frac{1}{3}+\frac{1}{3+2\delta}-\frac{1}{3+4\delta}-\frac{1}{3(1+2\delta)}\right), \tag{A21}$$

$$q_3=\frac{3}{8}\left(\frac{1}{3}-\frac{1}{3+2\delta}-\frac{1}{3+4\delta}+\frac{1}{3(1+2\delta)}\right), \tag{A22}$$

$$q_4=\frac{3}{8}\left(\frac{1}{3}-\frac{3}{3+2\delta}+\frac{3}{3+4\delta}-\frac{1}{3(1+2\delta)}\right), \tag{A23}$$

where $\delta=\nu_2/\nu_1$.