Drift Mobility and Diffusion for Impurities in Ionic Crystals

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An electric field exerts a force on the charged ions in an ionic crystal and causes a net flow of ions and vacancies. In calculations of the drift mobility μ and diffusion coefficient D, it has been customary to assume that the vacancy flow does not alter the average vacancy concentrations at sites that are second-nearest neighbors or farther from the impurity. In the present treatment, this approximation is avoided. Instead vacancies are presumed to be at equilibrium only at vacancy sources and sinks and on the symmetry plane containing the impurity. The resulting equations for μ/D include terms $\Sigma_i k_i \Delta w_i$. Here Δw_i is the difference between the vacancy-jump frequencies in the positive and negative x directions from site i in the absence of a field, and the k_i are coefficients. The summation, which is over all sites in the crystal, simplifies in a number of special cases. Whenever the vacancy-jump frequency for association of a vacancy-impurity complex differs from the vacancy-jump frequency far from an impurity, extra terms which have not appeared in previous expressions for μ/D are obtained.

INTRODUCTION

AN electric field E exerts a force on the ions in an ionic crystal. This force causes the ions to have a preferred direction of jump and will cause ions of a given species to undergo an average net displacement $\langle x\rangle = \mu E t$. Here t is the diffusion time and μ is the drift mobility of this species. The average displacement $\langle x\rangle$ can be measured by an experiment where a layer of radioactive tracer ions of the species is originally on a plane at $x=0$. Then $\langle x\rangle$ is the average x position of the tracer ions after time t. This can be determined directly from the position of the center of the tracer profile, since in a homogeneous crystal with a constant field E this profile will be symmetric around its midpoint.

If each tracer jump is independent of the directions of preceding jumps, the simple Nernst-Einstein relation,[1] $\mu kT = Dq$, relates the drift mobility of the given species to its tracer diffusion coefficient D. Here, q is the net ionic charge, k is Boltzmann's constant, and T is the absolute temperature. When diffusion occurs by a vacancy mechanism, however, the directions of successive ion jumps are not independent of one another. McCombie and Lidiard[2] showed that for self-diffusion by a vacancy mechanism, the factor D in the Nernst-Einstein relation must be replaced by Df^{-1}, where f is the correlation factor. Subsequent work[3–5] has shown that for impurity diffusion the additional factor is not simply f but instead is a somewhat different function of the vacancy-jump frequencies near the impurity. These calculations of μ/D for impurity diffusion have all assumed that the vacancy concentrations at sites which are second-nearest neighbors or farther from the impurity are maintained at their equilibrium values. In the present calculations, this restriction is removed. This introduces a number of additional terms into the expression for μ/D. Even in very simple cases, these terms can be important.

[1] See, e.g., A. B. Lidiard, *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1957), Vol. 20, p. 324.
[2] C. W. McCombie and A. B. Lidiard, Phys. Rev. **101**, 1210 (1956).
[3] A. B. Lidiard, *Reactivity of Solids*, edited by J. H. de Boer *et al.* (Elsevier Publishing Company, Amsterdam, 1961), p. 52.
[4] R. E. Howard and A. B. Lidiard, J. Phys. Soc. Japan Suppl. **18**, 197 (1963).
[5] J. R. Manning, Phys. Rev. **125**, 103 (1962).

BASIC EQUATIONS

In a preceding paper,[6] diffusion with a driving force was discussed in terms of effective jump frequencies. This approach considers planar diffusion normal to certain planes (usually the more nearly close-packed planes) through which an atom cannot pass directly in one jump. In passing from one side of such a plane to the other, the atom at some time must stop briefly at a site on this plane. An example of a suitable direction is the [100] direction in a face-centered cubic structure. Here neighboring (100) planes are equally spaced at a distance d, with d equal to half the length of a unit cell edge or $\frac{1}{2}\sqrt{2}$ times the nearest-neighbor distance in an fcc crystal.

In any crystal with equally spaced planes, the average atom drift velocity $\langle v\rangle$ for diffusion normal to these planes was found to be

$$\langle v\rangle = 2Dd^{-1}(A+B+\tfrac{1}{2}d\partial \ln f/\partial x), \qquad (1)$$

where D is the tracer diffusion coefficient in the absence of any forces, d is the distance between neighboring planes, and A and B are proportional to the driving force. In the present discussion, we shall assume there is no variation of diffusion coefficient with position. Then $\partial \ln f/\partial x$ equals zero. The direct effect of the force on the energy of motion for a diffusing atom is given by A; while for diffusion by a vacancy mechanism, B gives the indirect effect from a flow of vacancies. This flow results from the action of the force on the other atoms in the crystal.

In particular, A is given by[6]

$$\nu_{0+b} = \nu_{0b}(1+A), \qquad (2)$$

where ν_{0+b} is the basic jump frequency for a jump from

[6] J. R. Manning, Phys. Rev. **139**, A126 (1965); *ibid.* **124**, 470 (1961).

a site on plane 0 to one of the neighboring sites on plane +1 immediately on the right (+x direction) of plane 0, and ν_{0b} is this same quantity in the absence of driving forces. By definition[6] of ν_{0+b},

$$\nu_{0+b}=w_{T0+}N_{v+}, \tag{3}$$

where N_{v+} is the equilibrium probability (in the absence of driving forces) that a site which is on plane +1, and neighbors on our diffusing tracer atom, will contain a vacancy; while w_{T0+} is the jump frequency for the atom on plane 0 when there is a vacancy at a neighboring site on plane +1. The force by definition does not affect N_{v+} but can affect the energy of motion which determines w_{T0+}.

When the driving force is that from an electric field, the usual approximation is that the force decreases the energy of motion for a w_{T0+} jump in the direction of the field by $\Delta E_m=\frac{1}{2}q_tEd$, where q_t is the electric charge of the tracer and E is the magnitude of the electric field. Then, $\nu_{0+b}/\nu_{0b}=\exp(\Delta E_m/kT)$; and to first order

$$A=\frac{q_tEd}{2kT}. \tag{4}$$

The expression for B is[6]

$$B=\frac{\nu_{\alpha+}}{N_{v+}w_{\beta+}}-1, \tag{5}$$

where $w_{\beta+}$ is the effective escape or randomization frequency for a vacancy which is on a site j. Here site j is on plane +1 and neighbors on the tracer (which is on plane 0). The vacancy can randomize its position with respect to the tracer by making a series of one or more jumps which takes it to a site on plane 0 without exchanging with the tracer. By definition, $w_{\beta+}$ is the frequency with which the vacancy follows a path carrying it either to plane 0 or else to an infinite distance from the tracer without having either exchanged with the tracer or returned to one of the sites on plane +1 neighboring on the tracer. The number of jumps in the series can be any number from one to infinity. When there are sources and sinks for vacancies in the crystal, this definition can be revised to state that a vacancy need merely reach either plane 0 or a sink where it is destroyed. In practice of course, the vacancy will never move an infinite distance away. The important point is that it not return to a site on plane +1 neighboring on the tracer or exchange with the tracer. Similarly, $\nu_{\alpha+}$ is the frequency with which "fresh vacancies," which either have never exchanged with the tracer or else have arrived at a site on plane 0 since their last such exchange, arrive at a site on plane +1 neighboring on the tracer.

Vacancies which contribute to $\nu_{\alpha+}$ follow exactly the reverse of the paths for vacancies which contribute to $w_{\beta+}$. In the absence of driving forces, a vacancy is just as likely to move in one direction along a path as in the opposite direction. The term $N_{v+}w_{\beta+}$ gives the frequency of vacancy travel on these paths away from the sites on plane +1 while the term $\nu_{\alpha+}$ gives the frequency of travel in the other direction. Thus, in the absence of forces $\nu_{\alpha+}$ equals $N_{v+}w_{\beta+}$ and B equals zero.

If site p is any site either on plane 0 or next to a vacancy source or sink, and site j is one of the sites on plane +1 neighboring on the tracer (let us assume that there are Z such sites all equivalent to one another), we can write

$$\nu_{\alpha+}=Z\sum_p N_{vp}w_{pj}, \tag{6}$$

where N_{vp} is the average probability that there is a vacancy at site p and w_{pj} is the frequency with which such a vacancy follows a path taking it to a site j without returning to any site p. A driving force will not change the value of N_{vp} since a vacancy source or sink should always keep the vacancy concentration at neighboring sites at its equilibrium value. Also because of the symmetry around plane 0, deviations in the vacancy flow near the tracer (impurity) average out to zero on this plane.

For vacancies moving in the opposite direction

$$N_{v+}w_{\beta+}=ZN_{vj}\sum_p w_{jp}, \tag{7}$$

where N_{vj} is the average probability that a vacancy is at site j in the absence of a force, and w_{jp} is the frequency with which a vacancy which is at this site begins a path to take it to a site p without exchanging with the tracer or returning to any site j.

The frequency w_i for a given jump i in an electric field can be expressed in terms of the frequency w_{i0} in the absence of a field by an equation,

$$w_i=w_{i0}(1+\epsilon_i). \tag{8}$$

If there is a uniform field E directed along the x axis and the component of the vacancy jump in the direction of the field is Δx_i, one finds to first order

$$\epsilon_i=\frac{-q_sE(\Delta x_i)}{2kT}, \tag{9}$$

where q_s is the charge of the solvent atom involved in the jump. In most cases of interest, ϵ_i is much less than one. A number of jumps i will make up the paths between any sites j and p. Thus, one can write

$$w_{jp}=w_{jp0}[1+\epsilon_{jp}], \tag{10}$$

where w_{jp0} is the value of w_{jp} in the absence of the field, and to first order

$$\epsilon_{jp}=\sum_i \epsilon_i. \tag{11}$$

Here the sum is over all jumps in the path j-p, and we assume that the ϵ_i are small enough so that ϵ_{jp} also is much less than one. The sum of Δx_i along the path j-p

equals $n_{jp}d$, where n_{jp} is the number of jumps in the $+x$ direction which a vacancy must take to move from plane $+1$ containing site j to the plane containing site p. When q_s, E, and T are the same for each jump along the path j-p, one finds for any path between sites j and p,

$$\epsilon_{jp}=-(q_sEd/2kT)n_{jp}. \tag{12}$$

For jumps in the opposite direction along the path j-p,

$$w_{pj}=w_{pj0}(1-\epsilon_{jp}), \tag{13}$$

where w_{pj0} is the value of w_{pj} in the absence of the field. Dividing Eq. (6) by Eq. (7) then gives

$$\frac{\nu_{\alpha+}}{N_{v+}w_{\beta+}}=\frac{\sum_p N_{vp}w_{pj0}(1-\epsilon_{jp})}{\sum_p N_{vj}w_{jp0}(1+\epsilon_{jp})}. \tag{14}$$

Since N_{vp} and N_{vj} are probabilities (or vacancy concentrations) in the absence of the field

$$N_{vj}w_{jp0}=N_{vp}w_{pj0}, \tag{15}$$

and to first order in ϵ_{jp},

$$\frac{\nu_{\alpha+}}{N_{v+}w_{\beta+}}=1-\frac{2\sum_p w_{jp0}\epsilon_{jp}}{\sum_p w_{jp0}}. \tag{16}$$

Thus

$$B=(q_sEd/kT)\langle n_{jp}\rangle, \tag{17}$$

where

$$\langle n_{jp}\rangle=\frac{\sum_p w_{jp0}n_{jp}}{\sum_p w_{jp0}}. \tag{18}$$

Here $\langle n_{jp}\rangle$ represents the average number of steps a vacancy is to the right of plane $+1$ when it arrives at a vacancy sink or at a site on plane 0. Since the expression for $\langle n_{jp}\rangle$ contains the jump frequencies w_{jp0} in the absence of an electric field, $\langle n_{jp}\rangle$ also must be evaluated for a vacancy diffusing in the absence of an electric field. It may be noted that $n_{jp}=-1$ for vacancies which arrive at plane 0. For vacancies which arrive at sinks, n_{jp} may range from 0 to ∞.

Substituting Eqs. (4) and (17) into Eq. (1) gives

$$\langle v\rangle=(DE/kT)(q_t+2q_s\langle n_{jp}\rangle). \tag{19}$$

The drift mobility μ equals the average velocity in unit electric field. Thus,

$$\mu=\langle v\rangle E^{-1} \tag{20}$$

and

$$\mu/D=(q_t/kT)(1+(2q_s/q_t)\langle n_{jp}\rangle). \tag{21}$$

The first term inside the parentheses arises from the direct force exerted by the field on the charged tracer ion. The second term gives the effect from the flow of vacancies created by the field. This second term makes our equations deviate from the simple Nernst-Einstein equation, $\mu/D=q_t/kT$.

Equation (21) is similar to that found in a previous paper,[5] where it was assumed that vacancies were maintained at equilibrium at sites which were second-nearest neighbors or farther from the impurity. In the present derivation, this assumption is avoided. Thus $\langle n_{jp}\rangle$ appears in the place where the quantity L appeared previously. In certain cases $\langle n_{jp}\rangle$ exactly equals L; normally however $\langle n_{jp}\rangle$ contains a number of terms not included in L.

CALCULATION OF $\langle n_{ip}\rangle$

Except when site j is very near a sink, very little error is introduced by assuming that the vacancy sinks are uniformly located on a sphere centered at the tracer and with a very large radius. With this assumption, we can proceed to calculate $\langle n_{jp}\rangle$.

The only vacancies which contribute to $w_{\beta+}$ are those which move from a site j to some site p (either on plane 0 or next to a sink) without exchanging with the tracer or arriving back at one of the sites j. Thus, these are the only vacancies which should be considered in calculating $\langle n_{jp}\rangle$. One can imagine the vacancy starting on a j site, with sinks on a hemisphere and the zero plane. Also interchange with the tracer is excluded. Then one imagines the vacancy "diffusing" to the sinks by a process averaged over all paths. Each site i in the system makes a contribution to $\sum w_{jp0}n_{jp}$. This contribution is the product of the net probability of the vacancy moving a step to the right each time it lands on that site multiplied by the average number of times it does land there. By summing over all sites i, $\sum w_{jp0}n_{jp}$ can be calculated. After the original jump, sites j also are treated as being sinks since paths which return the vacancy to a site j should be excluded from consideration. (These paths actually are included in our equations until the first return to a site j. This does not affect the calculated value of $\sum w_{jp0}n_{jp}$, however, since in moving from j to j the vacancy undergoes zero net x displacement.)

The contribution to $\sum w_{jp0}n_{jp}$ from a jump from site i is on the average

$$C_i=(w_{i+}-w_{i-})/R_i, \tag{22}$$

where w_{i+} is the frequency of jumps from site i which change the x displacement of the vacancy by $+d$ and w_{i-} is the frequency of jumps which make a change $-d$. Jumps involving the tracer do not contribute to w_{i+} or w_{i-} since by definition of w_{jp} the vacancy's path from site j to equilibrium site p cannot involve an exchange with the tracer. Also R_i is the total jump frequency from site i, so that w_{i+}/R_i is the probability of $+d$ and w_{i-}/R_i is the probability of $-d$. By definition,

$$R_i=\sum_k w_{ik}, \tag{23}$$

where w_{ik} is the vacancy-jump frequency from site i to a neighboring site k. The summation is over all sites k not occupied by the tracer.

If V_i is the average number of times a vacancy which starts at site j visits site i without reaching an equilibrium site p or returning to a site j neighboring on the tracer, one can write for the numerator in Eq. (18),

$$\sum_p w_{jp0}n_{jp}=R_1\sum_i C_iV_i. \tag{24}$$

Here R_1 is the total vacancy-jump frequency from site j to neighboring sites s with jumps involving the tracer excluded,

$$R_1=\sum_{s=1}^{z-1} w_{js}. \tag{25}$$

Both R_1 and the C_i are easily expressed in terms of vacancy-jump frequencies. To find $\langle n_{jp}\rangle$, one need calculate only the V_i and the frequency $\sum_p w_{jp0}$, which is the effective escape or randomization frequency in the absence of a field.

Sets of Equivalent Sites

In cubic crystals with diffusion along a ⟨100⟩ direction, all sites j neighboring on the tracer and on the plane to the right of the tracer are equivalent sites. A vacancy at any of these sites has the same effect on diffusion along the x axis as a vacancy at any other of these sites. Thus, they can be grouped together into a set of equivalent sites which we shall call set 1. Similarly, other sites on planes to the right of the tracer can be grouped into various sets which we shall number from 2 to ∞.

Considering the individual sites in terms of sets simplifies the problem. Equations (22)–(25) are still valid. However, V_i in these equations now refers to the total number of visits summed over all sites in set i; and the vacancy-jump frequencies w_{ik} refer to the total frequency of jumps to all of the various sites in set k from a particular site in set i, summed over all sites in set k. Also, jumps between two sites in the same set do not influence diffusion along the x axis. Thus, the w_{ii} and contributions of these jumps to the R_i can for our purposes be treated as equal to zero. The V_i for the various sets i then can be calculated as follows.

Number of Vacancy Visits per Set

The sites on plane 0 are all equilibrium sites p. Thus, the only sites i which give a contribution to $\sum w_{jp0}n_{jp}$ are those included in sets 1 to ∞. The values of V_i for these sites can be obtained from the equations,

$$V_1=1, \tag{26}$$

$$V_i=(w_{1i}/R_1)V_1+\sum_{k\neq i}(w_{ki}/R_k)V_k \quad \text{with} \quad i,k=2,\cdots,n, \tag{27}$$

where the number of sets n goes to infinity. These simultaneous equations can be solved for the $V_i(i=1,\cdots,n)$ by use of determinants. This yields

$$V_i=a_ib^{-1}. \tag{28}$$

Since n goes to infinity, both a_i and b are determinants of infinite order,

$$b=\begin{vmatrix} +1 & 0 & 0 & \cdots & 0 \\ -w_{12}R_1^{-1} & +1 & -w_{32}R_3^{-1} & \cdots & -w_{n2}R_n^{-1} \\ -w_{13}R_1^{-1} & -w_{23}R_2^{-1} & +1 & \cdots & -w_{n3}R_n^{-1} \\ \vdots & \vdots & \vdots & & \vdots \\ -w_{1n}R_1 & -w_{2n}R_2 & -w_{3n}R_3 & \cdots & +1 \end{vmatrix} \tag{29}$$

and a_i is just b with the ith column replaced with $\{1,0,0,0,\cdots\}$. Also,

$$\sum_i C_iV_i=\Omega b^{-1}, \tag{30}$$

where

$$\Omega=\begin{vmatrix} C_1 & C_2 & C_3 & \cdots & C_n \\ -w_{12}R_1^{-1} & +1 & -w_{32}R_3^{-1} & \cdots & -w_{n2}R_n^{-1} \\ -w_{13}R_1^{-1} & -w_{23}R_2^{-1} & +1 & \cdots & -w_{n3}R_n^{-1} \\ \vdots & \vdots & \vdots & & \vdots \\ -w_{1n}R_1^{-1} & -w_{2n}R_2^{-1} & -w_{3n}R_3^{-1} & \cdots & +1 \end{vmatrix} \tag{31}$$

and the numerator in Eq. (18) can be expressed in terms of the infinite-order determinants Ω and b,

$$\sum_p w_{jp0}n_{jp}=R_1\Omega b^{-1}. \tag{32}$$

CALCULATION OF EFFECTIVE ESCAPE FREQUENCY $\sum_p w_{jp0}$

The effective escape frequency, which appears in the denominator of Eq. (18), can be calculated in terms of similar infinite-order determinants. The effective escape frequency from site $j(\sum_p w_{jp0})$ is smaller than the jump frequency R_1 since some vacancies which make w_{1i} jumps from site j (in set 1) to neighboring sites in set i return again to a site in set 1 before arriving at an equilibrium site p. These vacancies contribute to R_1 but not to $\sum_p w_{jp0}$,

$$\sum_p w_{jp0}=\sum_{p=1}^{\rho} w_{1p}+\sum_{i=2}^{n} w_{1i}\left[1-\sum_{k=2}^{n} V_{k(i)}\frac{w_{k1}}{R_k}\right]. \tag{33}$$

Here the summation over p includes all sites p (on plane 0) which can be reached in one jump from site j and are not occupied by the tracer, and w_{1p} is the jump frequency to such a site. Also, w_{1i} is the jump frequency to other sets neighboring on site j, and $V_{k(i)}$ is the number of times a vacancy which starts on set i will visit set k without reaching a site p or 1. The summation over k gives the probability that a vacancy which makes a w_{1i} jump will return to set 1 before reaching a site p. The fraction w_{k1}/R_k is the probability of this happening immediately after a given visit to set k. As in the previous section, all jump frequencies are those in the

absence of a field. The $V_{k(i)}$ are given by

$$V_{k(i)}=\delta_{ki}+\sum_{m\neq k} V_{m(i)}(w_{mk}/R_m), \quad m,k=2,\cdots,n, \quad (34)$$

where δ_{ki} is unity if $k=i$ and zero otherwise. Solving Eq. (34) for the $V_{k(i)}$ (with $k=2,\cdots,\infty$) gives

$$V_{k(i)}=Q_{k(i)}\pi^{-1}. \quad (35)$$

When the number of sets n goes to infinity, both $Q_{k(i)}$ and π are determinants of infinite order,

$$\pi=\begin{vmatrix} +1 & -w_{32}R_3^{-1} & \cdots & -w_{n2}R_n^{-1} \\ -w_{23}R_2^{-1} & +1 & \cdots & -w_{n3}R_n^{-1} \\ \vdots & \vdots & & \vdots \\ -w_{2n}R_2^{-1} & -w_{3n}R_3^{-1} & \cdots & +1 \end{vmatrix} \quad (36)$$

and $Q_{k(i)}$ is found from π by replacing the kth column of π by $\{0,0,\cdots,0,1,0,\cdots,0\}$, where the nonzero element is in the ith row. Using these expressions for $Q_{k(i)}$, we find

$$-\sum_{k=2}^{n} V_{k(i)}w_{k1}R_k^{-1}=H_i\pi^{-1}, \quad (37)$$

where H_i is just π with the ith row replaced by $(-w_{21}R_2^{-1}, -w_{31}R_3^{-1}, \cdots, -w_{n1}R^{-1})$. Now

$$\sum_{i=2}^{n} w_{1i}H_i\pi^{-1}=\sigma, \quad (38)$$

where

$$\pi\sigma=\begin{vmatrix} 0 & -w_{21}R_2^{-1} & -w_{31}R_3^{-1} & \cdots & -w_{n1}R_n^{-1} \\ -w_{12} & +1 & -w_{32}R_3^{-1} & \cdots & -w_{n2}R_n^{-1} \\ -w_{13} & -w_{23}R_2^{-1} & +1 & \cdots & -w_{n3}R_n^{-1} \\ \vdots & \vdots & \vdots & & \vdots \\ -w_{1n} & -w_{2n}R_2^{-1} & -w_{3n}R_3^{-1} & \cdots & +1 \end{vmatrix}. \quad (39)$$

Since

$$R_1=\sum_{p=1}^{\rho} w_{1p}+\sum_{i=2}^{n} w_{1i}, \quad (40)$$

Eq. (33) reduces to the simple expression

$$\textstyle\sum_p w_{jp0}=R_1+\sigma. \quad (41)$$

By direct multiplication, we find

$$\pi R_1=\begin{vmatrix} R_1 & 0 & 0 & \cdots & 0 \\ 0 & +1 & -w_{32}R_3^{-1} & \cdots & -w_{n2}R_n^{-1} \\ 0 & -w_{23}R_2^{-1} & +1 & \cdots & -w_{n3}R_n^{-1} \\ \vdots & \vdots & \vdots & & \vdots \\ 0 & -w_{2n}R_2^{-1} & -w_{3n}R_3^{-1} & \cdots & +1 \end{vmatrix}. \quad (42)$$

Then, adding Eqs. (39) and (42) gives

$$\textstyle\sum_p w_{jp0}=\pi^{-1}R_1\Phi, \quad (43)$$

where

$$\Phi=\begin{vmatrix} +1 & -w_{21}R_2^{-1} & -w_{31}R_3^{-1} & \cdots & -w_{n1}R_n^{-1} \\ -w_{12}R_1^{-1} & +1 & -w_{32}R_3^{-1} & \cdots & -w_{n2}R_n^{-1} \\ -w_{13}R_1^{-1} & -w_{23}R_2^{-1} & +1 & \cdots & -w_{n3}R_n^{-1} \\ \vdots & \vdots & \vdots & & \vdots \\ -w_{1n}R_1^{-1} & -w_{2n}R_2^{-1} & -w_{3n}R_3^{-1} & \cdots & +1 \end{vmatrix}. \quad (44)$$

Because of the zeros in the first row of the determinant b in Eq. (29), b exactly equals π as given in Eq. (36). From Eqs. (18), (32), and (43), it then follows that

$$\langle n_{jp}\rangle=\Omega\Phi^{-1}. \quad (45)$$

EVALUATION OF Φ AND Ω

If we let m_i be the minor of the element in the first row and ith column of Φ (or Ω) and let $M_i=m_i(-1)^{i+1}$, we find after expanding Φ in terms of minors

$$\Phi=M_1-\sum_{i=2}^{n} w_{i1}M_iR_i^{-1}. \quad (46)$$

Since π equals M_1, Eq. (43) yields

$$\sum_p w_{jp0}=R_1-\sum_{i=2}^{n}\frac{R_1}{R_i}\frac{M_i}{M_1}w_{i1}. \quad (47)$$

The w_{i1} and w_{1i} will equal zero for all n greater than some value q (i.e., the sites $i=2,\cdots,q$ are the only i sites which can be reached in one jump from site 1). Then, with Eq. (40), we find

$$\sum_p w_{jp0}=\sum_{p=1}^{\rho} w_{1p}+\sum_{i=2}^{q} w_{1i}F_i, \quad (48)$$

where

$$F_i=1-\frac{w_{i1}}{w_{1i}}\frac{R_1}{R_i}\frac{M_i}{M_1} \quad \text{for} \quad i=2,\cdots,q. \quad (49)$$

In calculations of the correlation factor, $\sum_p w_{jp0}$ is often expressed in the form of Eq. (48). In such calculations, numerical values of the F_i have been found for a number of cubic structures with various vacancy-jump frequencies in the vicinity of the impurity.

When Ω is expanded in terms of minors, we find

$$\Omega=\sum_{i=1}^{n} C_iM_i=\sum_{i=1}^{n}\Delta w_iM_iR_i^{-1}, \quad (50)$$

where

$$\Delta w_i=w_{i+}-w_{i-}. \quad (51)$$

With $\Phi=M_1R_1^{-1}\sum_p w_{jp0}$, as in Eq. (43), we find

$$\langle n_{jp}\rangle=\frac{\Delta w_1+\sum_{i=2}^{q}\Delta w_i\frac{w_{1i}}{w_{i1}}(1-F_i)+\sum_{i=q+1}^{n}\Delta w_i\frac{R_1}{R_i}\frac{M_i}{M_1}}{\sum_{p=1}^{\rho} w_{1p}+\sum_{i=2}^{q} w_{1i}F_i}. \quad (52)$$

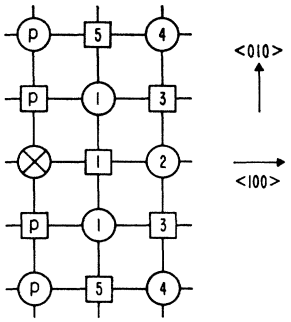

FIG. 1. Location of sites in sets 1 to 5 in a face-centered cubic sublattice. The impurity site is marked X. Plane 0 is the vertical plane through this site. Sites marked by circles are in the plane of the paper. Sites marked by squares are a distance d above or below this plane. In addition there are four sites in set 5 which are not shown. These sites are a distance $2d$ above or below the circled sites in set 1. Two additional sites in set 4 are $2d$ above or below the circled site in set 2.

Equation (52) is valid for any cubic structure. When substituted into Eq. (21), it yields a general expression for μ/D.

In a number of special cases, Eq. (52) simplifies. If the presence of the impurity does not affect vacancy jumps which originate at sites on the third coordination shell or farther from the impurity, the Δw_i for $i \geq q+1$ will all be zero. The frequency of jumps w_{i+} in the $+x$ direction (away from the impurity) equals the frequency of jumps w_i in the $-x$ direction (toward the plane containing the impurity). This makes $(w_{i+}-w_{i-})$ and hence Δw_i equal zero for these sites. The summation over i from $q+1$ to n then equals zero and Eq. (52) reduces to

$$\langle n_{jp}\rangle = \frac{\Delta w_1 + \sum_{i=2}^{q} \Delta w_i (w_{1i}/w_{i1})(1-F_i)}{\sum_{p=1}^{\rho} w_{1p} + \sum_{i=2}^{q} w_{1i} F_i} . \quad (53)$$

If a vacancy at site i is bound to the impurity with a nonzero binding energy, Δw_i for this site probably will not equal zero. Still, one expects the Δw_i for sites $i>q$ to be smaller than the Δw_i for sites $i \leq q$, which are closer to the impurity. Thus, in spite of nonzero binding energies and Δw_i's for $i>q$, Eq. (53) may be a good approximation in many cases.

If all vacancy jumps involving solvent ions have the same jump frequency, all Δw_i for $i \geq 2$ will be zero. However, Δw_1 will not be zero since jumps involving the tracer ion are excluded in calculating the w_{i+} and w_{i-}. From a site in set 1, one of the vacancy jumps in the $-x$ direction would involve an exchange with the tracer. Hence Δw_1 in the present case equals w, where w is the vacancy-jump frequency for exchange with a solvent ion, and Eqs. (48) and (52) yield

$$\langle n_{jp}\rangle = w[\textstyle\sum_p w_{jp0}]^{-1} . \quad (54)$$

This expression also applies to self diffusion where the solvent jump frequency w equals the tracer jump frequency w_2. In cubic crystals, the tracer correlation factor f is given by[7]

$$f = \frac{\sum_p w_{jp0}}{2w_2 + \sum_p w_{jp0}} . \quad (55)$$

In the special case where $w=w_2$, $1+2\langle n_{jp}\rangle$ equals f^{-1}. For self-diffusion, q_s of course equals q_t, and Eq. (21) reduces simply to

$$(\mu/D) = (q_t/kTf) , \quad (56)$$

as expected.[2]

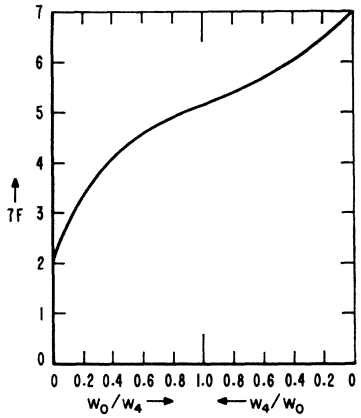

FIG. 2. $7F$ as a function of w_4/w_0 and w_0/w_4.

The accurate evaluation of $\langle n_{jp}\rangle$ from Eq. (52) when Δw_i does not equal zero for $i>q$ requires calculation of the M_i for $i>q$. This in turn involves evaluating a determinant containing a very large number of terms. If, however, we restrict consideration to cases where $\Delta w_i \neq 0$ only for $i \leq q$, we can use Eq. (53). Here the M_i are expressed completely in terms of the F_i, which in many cases have already been determined from calculations of the correlation factor. As an example, let us consider the NaCl structure.

APPLICATION TO NaCl STRUCTURE

Each sublattice in the NaCl structure is face-centered cubic. Vacancy-jump frequencies near an impurity in a face-centered cubic lattice can be defined as follows: w_1 is the jump frequency for a jump between two nearest neighbors of the impurity, w_2 for exchange with the impurity, w_3 for a jump from a nearest-neighbor site to a non-nearest neighbor site, w_4 for the reverse of a w_3 jump, and w_0 for any other jump. Sites in set 1 and neighboring sites in sets 2 to 5 are shown in Fig. 1. It can be seen that

$$\begin{aligned} \Delta w_1 &= 3w_3 - 2w_1 , \\ \Delta w_2 &= 4w_0 - 4w_4 , \\ \Delta w_3 &= 2w_0 - 2w_4 , \\ \Delta w_4 &= w_0 - w_4 , \\ \Delta w_5 &= w_0 - w_4 , \end{aligned} \quad (57)$$

[7] J. R. Manning, Phys. Rev. **136**, A1758 (1964).

and all other Δw_i equal zero. In Eq. (53), w_{gh} is the total jump frequency to sites in set h from a particular site in set g (summed over all sites in set h). Thus,

$$\begin{aligned} w_{12}&=w_3, \quad & w_{21}&=4w_4, \\ w_{13}&=2w_3, \quad & w_{31}&=2w_4, \\ w_{14}&=w_3, \quad & w_{41}&=w_4, \\ w_{15}&=2w_3, \quad & w_{51}&=w_4. \end{aligned} \tag{58}$$

In addition,

$$\sum_p w_{1p}=2w_1+w_3. \tag{59}$$

Substituting these values into Eq. (53) gives

$$\langle n_{jp}\rangle=\frac{3w_3-2w_1-w_3[(w_4-w_0)/w_1]7(1-F)}{2w_1+7Fw_3}, \tag{60}$$

where

$$7F=1+F_2+2F_3+F_4+2F_5. \tag{61}$$

The factor $7F$ has been calculated previously, assuming vacancy-jump frequencies w_0, w_1, w_2, w_3, and w_4 as above.[7] This factor depends only on the ratio w_4/w_0 and varies between the values 2 and 7, as shown in Fig. 2. When $w_4=w_0$, $7F$ equals approximately 5.15.

For a monovalent positively charged impurity ion diffusing in a monovalent sublattice, $q_i=q_s=e$. Substituting Eq. (60) for $\langle n_{jp}\rangle$ into Eq. (21) gives

$$\frac{\mu}{D}=\frac{e}{kT}\frac{-2w_1+\varphi_1 w_3}{2w_1+7Fw_3}, \tag{62}$$

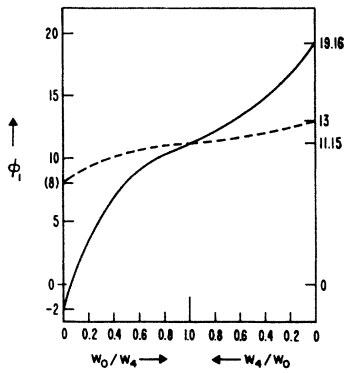

FIG. 3. The solid line gives φ_1 as a function of w_4/w_0 and w_0/w_4. The dashed line gives values obtained if terms proportional to w_4-w_0 are neglected.

where

$$\varphi_1=6+7F-14(1-F)(w_4-w_0)w_4^{-1}. \tag{63}$$

For a divalent impurity ($q_i=2e$) in a monovalent sublattice ($q_s=e$), we find

$$\frac{\mu}{D}=\frac{2e}{kT}\frac{\varphi_2 w_3}{2w_1+7Fw_3}, \tag{64}$$

where

$$\varphi_2=3+7F-7(1-F)(w_4-w_0)w_4^{-1}. \tag{65}$$

In Figs. 3 and 4, the solid lines give φ_1 and φ_2 as a function of w_0/w_4. It may be noted that φ_2 and hence μ/D for a divalent impurity goes to zero when w_0/w_4 goes to zero. In this limit the vacancy can never completely dissociate from the impurity. Each w_3 jump is necessarily followed by a w_4 jump which returns the vacancy to a site neighboring on the impurity, giving a permanently bound vacancy-divalent impurity complex. Moving the complex from sites a-b to sites c-d and replacing it with two monovalent ions moved from sites c-d to a-b results in no net flux of charge. Thus, the force tending to move this complex is zero and μ should equal zero for a permanently bound complex. Also in the limit where w_0/w_4 goes to zero, φ_1 goes to -2 and $7F$ to $+2$. Thus, for a monovalent impurity, μ/D equals $-e/kT$ in this limit, just the negative of the Nernst-Einstein relation. This also is the expected value. Interchanging a bound vacancy-monovalent impurity complex with two monovalent ions results in a net flux of charge $+e$ in a direction opposite to the motion of the complex. This gives the bound complex an effective charge $-e$.

In the opposite limit where w_4/w_0 equals zero, one finds to two decimal places that φ_1 becomes 19.16 and φ_2 becomes 13.08. For $w_4=w_0$, φ_1 equals 11.15 and φ_2 equals 8.15.

The present equations for φ_1 and φ_2 include terms proportional to w_4-w_0. These terms do not appear in previous treatments. They arise from the terms in Eq. (53) proportional to Δw_i for $i=2, \cdots, q$, where site i is on the second coordination shell. If these terms were not included, φ_1 and φ_2 would be given by the dashed lines in Figs. 3 and 4. These terms do not appear in previous treatments because sites on the second coordination shell in these treatments have always been assumed to have equilibrium vacancy concentrations. It is apparent that effects from these terms can be appreciable. For example, when $w_0/w_4=0$, the dashed lines for φ_1 and φ_2 deviate greatly from the correct values -2 and 0.

Expressions similar to Eqs. (62) and (64) have been found previously. Howard and Lidiard,[3,4] using a pair reorientation method with vacancy concentrations assumed to be at equilibrium on all sites on the second coordination shell from the impurity, found expressions of this form but with $7F=7$, $\varphi_1=13$, and $\varphi_2=10$. These correspond to values from the dashed lines in Figs. 3 and 4.

Previous calculations[5] using the present method but making the approximation that vacancy concentrations

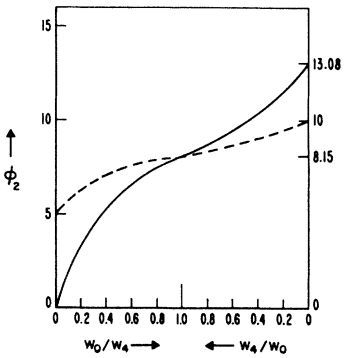

FIG. 4. The solid line gives φ_2 as a function of w_4/w_0 and w_0/w_4. The dashed line gives values obtained if terms proportional to w_4-w_0 are neglected.

(for vacancies which have never been at site j) are at equilibrium on the second coordination shell gave expressions of this same form but with $7F=5.15$, $\varphi_1=6+7F$, and $\varphi_2=3+7F$. These three expressions are valid in the special case where $w_4=w_0$. The essential difference between the present results and those in Ref. 5 is that $\langle n_{jp}\rangle$ in the present paper replaces the quantity L in Ref. 5. In the special case where $w_0=w_4$, L equals exactly $\langle n_{jp}\rangle$. Otherwise, L gives the values shown by the dashed lines in Figs. 3 and 4.

If the pair reorientation method is applied in its general form with allowance being made for vacancy-impurity pairs which are not nearest neighbors and vacancy concentrations are arbitrarily assumed to be at equilibrium only at an infinite distance from the impurity, results equivalent to those in the present paper are found. The detailed calculations require solution of n linear equations in n unknowns, where n goes to infinity. Thus, determinants of infinite order again are obtained. These expressions reduce exactly to Eqs. (21) and (52).

SPECIAL BINDING AT SECOND-NEAREST-NEIGHBOR SITE

In a face-centered cubic sublattice, a vacancy at a second-nearest-neighbor site from a divalent impurity may still be strongly bound to the impurity. Then, instead of the jump frequencies, w_0, w_1, w_2, w_3, and w_4 which were assumed above, a better approximation to the actual vacancy-jump frequencies might be to let w_2 be the frequency for exchange with the impurity w_1. For a jump from one nearest-neighbor site to another, let $w_{\beta i}$ be that from a first-nearest neighbor to a second-nearest neighbor, $w_{i\beta}$ from a second- to first-nearest neighbor, $w_{\beta m}$ from a first-nearest neighbor to other sites m which are not a first or second neighbor of the impurity, w_{im} from a second-nearest neighbor to a site m, and w_0 for all other vacancy jumps.

This gives

$$\begin{aligned}\Delta w_1&=3w_{\beta m}-2w_1,\\ \Delta w_2&=4w_{im}-4w_{i\beta},\end{aligned}\tag{66}$$

and all other Δw_i equal zero. Also

$$\begin{aligned}&w_{12}=w_{\beta i}, \qquad w_{21}=4w_{i\beta},\\ &w_{13}=w_{15}=2w_{\beta m}, \quad w_{14}=w_{\beta m},\\ &\textstyle\sum_p w_{1p}=2w_1+w_{\beta i}.\end{aligned}\tag{67}$$

Substituting these values into Eq. (52) gives

$$\langle n_{jp}\rangle=\frac{3w_{\beta m}-2w_1+2w_{\beta i}[(w_{im}-w_{i\beta})/w_{i\beta}](1-F_i)}{2w_1+2w_{\beta i}F_i+5w_{\beta m}F_m},\tag{68}$$

where

$$2F_i=1+F_2,\tag{69}$$

$$5F_m=2F_3+F_4+2F_5.\tag{70}$$

Both F_i and F_m have been calculated previously in terms of the above jump frequencies in correlation-factor calculations.[7] It was found that

$$2F_i=\frac{56.04+19.22(w_{i\beta}/w_{im})}{32.04+19.22(w_{i\beta}/w_{im})},\tag{71}$$

$$5F_m=\frac{121.72+66.99(w_{i\beta}/w_{im})}{32.04+19.22(w_{i\beta}/w_{im})}.\tag{72}$$

The jump frequencies between sites β, i, and m are related by the equation

$$w_{\beta i}/w_{\beta m}=w_{i\beta}/w_{im}.\tag{73}$$

This equation must be true if accumulation of vacancies at sites β, i, or m in the absence of driving forces is to be avoided. For a divalent impurity, $q_i=2e$. Then with $q_s=e$, it follows from Eqs. (21) and (68) that

$$\frac{\mu}{D}=\frac{2e}{kT}\frac{\varphi_3 w_{\beta m}}{2w_1+7F'w_{\beta m}},\tag{74}$$

where

$$\varphi_3=\frac{225.88+191.87(w_{\beta i}/w_{\beta m})}{32.04+19.22(w_{\beta i}/w_{\beta m})},\tag{75}$$

and

$$7F'=\frac{121.72+123.03(w_{\beta i}/w_{\beta m})+19.22(w_{\beta i}/w_{\beta m})^2}{32.04+19.22(w_{\beta i}/w_{\beta m})}.\tag{76}$$

When there is special binding at a second-nearest-neighbor site, one expects $w_{\beta i}$ to be much greater than $w_{\beta m}$. Then Eq. (74) becomes

$$\mu/D=(2e/kT)[9.98w_{\beta m}/(2w_1+w_{\beta i})].\tag{77}$$

There is some evidence in NaCl that a vacancy neighboring on a divalent Ca or Mn impurity ion has a jump frequency $w_{\beta i}$ much larger than w_1.[8,9] Then Eq. (77) would reduce to

$$\mu/D=(e/kT)(19.96w_{\beta m}/w_{\beta i})\tag{78}$$

and the ratio $w_{\beta m}/w_{\beta i}=w_{im}/w_{i\beta}$ can be calculated from a measurement of μ/D. The measured values at 700°C of $\mu/D\approx 0.07e/kT$ for Mn^{++} in NaCl [10] and of $\mu/D\approx 0.04e/kT$ for Ca^{++} in NaCl [11] gives

$$\begin{aligned}&w_{im}/w_{i\beta}\approx 0.0035 \quad \text{for } Mn^{++},\\ &w_{im}/w_{i\beta}\approx 0.002 \quad \text{for } Ca^{++}.\end{aligned}$$

According to this, the reassociation jump frequency $w_{i\beta}$ from site i is 300 to 500 times larger than that for dissociation w_{im}. The probability that the vacancy escapes from the impurity on any given jump thus is quite small.

[8] R. W. Dreyfus and R. B. Laibowitz, Phys. Rev. **135**, A1413 (1964).
[9] G. D. Watkins, Phys. Rev. **113**, 79, 91 (1959).
[10] B. G. Lur'e, A. N. Murin, and R. F. Brigevich, Fiz. Tverd. Tela **4**, 1957 (1962) [English transl.: Soviet Phys.—Solid State **4**, 1432 (1963)].
[11] S. N. Banasevich, B. G. Lur'e, and A. N. Murin, Fiz. Tverd. Tela **2**, 80 (1960) [English transl.: Soviet Phys.—Solid State **2**, 72(1960)].