

ACKNOWLEDGMENTS

The authors wish to express their sincere gratitude to Professor C. P. Slichter for his many helpful suggestions and for providing the opportunity to undertake this work. Thanks are extended to Professor G. S. Newell, who constructed with the authors the paramagnetic resonance spectrometer and contributed to the KCl fast-passage study. J. C. Bushnell and N. Fernelius

assisted in the analysis of the LiF data. The Cary spectrophotometer used in the optical studies was kindly made available by Professor R. J. Maurer. Stimulating discussions with other members of Professor Slichter's resonance group are gratefully acknowledged.

One of us (WCH) would like to thank Texas Instruments, Inc., where the LiF computer calculations were performed.

PHYSICAL REVIEW

VOLUME 125, NUMBER 1

JANUARY 1, 1962

Drift Mobility of an Ionic Impurity in an Electric Field

JOHN R. MANNING

National Bureau of Standards, Washington, D. C.

(Received August 21, 1961)

When diffusion occurs by either a vacancy or interstitialcy mechanism, an electric field has two effects on the diffusion process. First, the field exerts a direct force on the electrically charged ions. This effectively changes the energy of motion for an ion jump in the direction of the field. Secondly, the field causes a net flow of vacancies or interstitialcies. This makes vacancies or interstitialcies approach an ion more frequently from one direction and less frequently from the opposite direction. The drift mobility μ of an ionic impurity in an electric field is found from consideration of these two effects, with μ being related to D^* , the tracer diffusion coefficient of the impurity in the absence of an electric field. General equations are derived giving the value of μ/D^* in any homogeneous cubic crystal. Explicit expressions are calculated for several specific lattices. These equations apply best when the impurity ion has the same charge as the solvent ions in the sublattice of interest. Both vacancy and interstitialcy mechanisms are treated. The value of μ/D^* depends on both the diffusion mechanism and the relative values of the various jump frequencies near the impurity.

1. INTRODUCTION

IN ionic crystals, ions diffuse by making a series of discrete jumps from one lattice site to another. The tracer diffusion coefficient D^* depends on the frequency of random jumps in all possible directions. An electric field will cause the ions to jump more frequently in one direction than another, and the drift mobility μ depends on this excess frequency of jumps. When the excess frequency is related to the random frequency, μ will be related to D^* .

In a homogeneous crystal, both μ and D^* can be determined from a single tracer experiment. If a layer of tracer ions on a plane normal to an electric field E is allowed to diffuse for a time τ , the center of the tracer profile will shift a distance $\bar{x} = \mu E \tau$ toward one end of the specimen. When E and τ are known, a measurement of the shift \bar{x} allows one to calculate μ . The diffusion coefficient D^* can be found from the width of the tracer profile, which in a homogeneous crystal will be the same with or without a field.

In the present paper, results from a previous general treatment of diffusion in a gradient¹ are used to derive general expressions for μ/D^* in an electric field (electric potential gradient). Two separate contributions to the drift mobility are considered: (1) from the force the field exerts on the charged ions and (2) from the effect a flow

of vacancies or interstitialcies has on the diffusion process. Expressions applicable to any homogeneous cubic crystal and to either a vacancy or interstitialcy mechanism are obtained. Explicit results for several common lattices then are calculated from these expressions. The nonrandom return of dissociating vacancies is considered, so, for self-diffusion, the equations are exact.

Relations between μ and D^* have been obtained previously in several special cases. If the ions pursue a random walk in the absence of an electric field, μ/D^* is given by the simple Nernst-Einstein relation,²

$$\mu/D^* = q/kT, \quad (1)$$

where q is the charge of the diffusing ions, k is Boltzmann's constant, and T is the absolute temperature. In general however, the ions will not follow a random walk. Thus, a correlation factor f must be introduced,³ and Eq. (1) must be modified. McCombie and Lidiard⁴ pointed out that, for self-diffusion, the value of μ depends on the total jump frequency ν , while the tracer diffusion coefficient D^* depends on the fre-

² See e.g., A. B. Lidiard, in *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1957), Vol. 20, p. 324.

³ J. Bardeen and C. Herring, in *Atom Movements* (American Society for Metals, Cleveland, Ohio, 1951), p. 87; also in *Imperfections in Nearly Perfect Crystals* (John Wiley & Sons, Inc., New York, 1952), p. 261.

⁴ C. W. McCombie and A. B. Lidiard, *Phys. Rev.* **101**, 1210 (1956).

¹ J. R. Manning, *Phys. Rev.* **124**, 470 (1961).

quency νf . Thus, for self-diffusion by a vacancy mechanism, a factor f^{-1} must be introduced on the right-hand side of Eq. (1). For self-diffusion by an interstitialcy mechanism with collinear jumps, a factor $2f^{-1}$ must be introduced, the factor 2 arising because two ions participate in each interstitialcy jump. Howard and Lidiard studied the diffusion of an impurity in NaCl by considering the possible orientations of a vacancy-impurity complex.⁵ For an impurity which is diffusing by a vacancy mechanism in a face-centered cubic sublattice (NaCl lattice) and which has the same charge as the solvent ions in this sublattice, they found⁶

$$\frac{\mu}{D^*} \approx \frac{q}{kT} \left(\frac{-2w_1 + 13k_1}{2w_1 + 7k_1} \right), \quad (2)$$

where k_1 and w_1 are the jump frequencies for exchange of the vacancy with the various solvent ions surrounding it, the w_1 jumps being those in which the vacancy moves to another site neighboring on the impurity, and the k_1 jumps being those in which the vacancy moves away from the impurity.

The present treatment includes the above equations as special cases. However, it is considerably more general, including impurity diffusion in any homogeneous cubic crystal by either a vacancy or interstitialcy mechanism. This treatment applies best when the impurity has the same charge as the solvent ions in the sublattice containing the impurity.

2. DRIFT MOBILITY FOR A VACANCY MECHANISM

(a) Effect of an Electric Field

Since ions carry an electric charge, an electric field exerts a force on them. This changes the effective energy of motion for jumps in the direction of the field. The energy of motion for a jump is determined by the configuration at the barrier half-way between the initial and final ion positions. Thus, when diffusion occurs by a vacancy mechanism, the effective change in energy of motion equals half the change in electric potential energy resulting from the jump. The effective change δH_{oj} in the energy of motion for a tracer ion jump from site o to a neighboring site j is given by

$$\delta H_{oj} = -\frac{1}{2} q_t E \lambda \cos \phi_{oj}, \quad (3)$$

where q_t is the charge of the tracer, λ is the jump distance, and ϕ_{oj} is the angle between the electric field and the line o - j connecting site o to site j .

In addition to exerting a force directly on the charged tracer ions, the field may indirectly affect the diffusion process by causing a flow of vacancies or interstitialcies. When a vacancy flow occurs, vacancies approach an ion more frequently from one side than another. This changes the probability that the tracer will make an

uncorrelated jump to site j by a factor G_{oj} . In the Appendix, it is shown to a good approximation that, when an electric field causes a flow of vacancies in an ionic crystal with cubic symmetry,

$$G_{oj} = 1 + \frac{q_s E \lambda}{kT} L \cos \phi_{oj}, \quad (4)$$

where q_s is the charge of the solvent (nontracer) ions in the sublattice of interest, and L depends on the lattice geometry and the solvent ion jump frequencies in the region near the tracer. If certain simplifying assumptions are made about the vacancy jump frequencies, explicit values of L can be calculated. A general expression for L is given by Eq. (A7) in the Appendix, and several specific expressions are given in Table I.

(b) Drift Mobility

The drift mobility μ equals the drift velocity of an ion in unit electric field. The drift velocity \bar{v} in field E is given by

$$\bar{v} = \mu E. \quad (5)$$

In reference 1, it is found that for any type of gradient the mean ion drift velocity is given by

$$\bar{v} = 2D^* \lambda^{-1} [A + B + \frac{1}{2} \lambda (\partial \ln f / \partial x)]. \quad (6)$$

The quantity B is related to G_{oj} by the equation

$$G_{oj} = 1 + B \cos \phi_{oj}, \quad (7)$$

while, in a homogeneous crystal, A is given by

$$\nu_{ojb} = \nu_{ob} (1 + A \cos \phi_{oj}), \quad (8)$$

where ν_{ojb} is the basic ion jump frequency for a jump from site o to site j , and ν_{ob} is the basic ion jump frequency for a jump from site o in a direction normal to the field. The basic jump frequency is a theoretical quantity which can be calculated from the energies of motion and formation. In a homogeneous crystal, the energy of formation will be the same for ν_{obj} as for ν_{ob} . However, the energies of motion will differ by δH_{oj} . Thus,

$$1 + A \cos \phi_{oj} = \exp(-\delta H_{oj}/kT). \quad (9)$$

With the aid of Eq. (3), one finds to first order,

$$A = q_t E \lambda / 2kT. \quad (10)$$

From Eqs. (4) and (7), one finds

$$B = q_s E \lambda L / kT. \quad (11)$$

In the absence of concentration gradient effects, the correlation factor f does not depend on position,¹ so it follows from Eqs. (5) and (6) that

$$\mu/D^* = (q_t/kT) \{1 + 2Lq_s/q_t\}. \quad (12)$$

The factor in braces in Eq. (12) arises from the flow of vacancies. Since this factor can differ appreciably from

⁵ A. B. Lidiard, Phil. Mag. 46, 1218 (1955).

⁶ R. E. Howard and A. B. Lidiard (private communication).

TABLE I. Values of L in terms of the vacancy and interstitial jump frequencies.^{a-c}

Lattice	$\sum_{p=1}^{z-1} w_{jpa}$	$\sum_{p=1}^{z-1} w_{jpa} F_{jpa}$	$\sum_{p=1}^{z-1} w_{jpa} \cos\phi_p$	L
Vacancy mechanism				
Face-centered cubic	$4w_1+7k_1$	$2w_1+5.15k_1$	$-2w_1+3k_1$	$(-2w_1+3k_1)/(2w_1+5.15k_1)$
Diamond	$3w_1$	$2w_1$	w_1	$\frac{1}{3}$
Body-centered cubic	$3w_1+4k_1$	$2.35w_1+2.98k_1$	$-w_1+2k_1$	$(-w_1+2k_1)/(2.35w_1+2.98k_1)$
Simple cubic	$4w_1+k_1$	$3.04w_1+0.73k_1$	k_1	$k_1/(3.04w_1+0.73k_1)$
Interstitialcy mechanism (with collinear jumps)				
NaCl (or AgCl)	$3w_1$	$2w_1$	w_1	$\frac{1}{3}$
Ca sublattice in CaF ₂ , fluorite (same as fcc)	$4w_1+k_1$	$3.26w_1+0.74k_1$	k_1	$k_1/(3.26w_1+0.74k_1)$

^a Values of w_{jpa} are defined as follows: For diffusion by a vacancy mechanism in a face-centered cubic lattice, w_1 is the frequency with which a vacancy will jump from one site neighboring on an impurity to another given site neighboring on this impurity (nondissociative jump), and k_1 is the frequency with which a vacancy will jump from a site neighboring on an impurity to a given one of the adjacent sites not neighboring on the impurity (dissociative jump). For the other lattices, w_1 is the frequency with which a vacancy or interstitialcy will jump from a site which is a nearest neighbor of an impurity to one of the group of second nearest neighbors sites, and k_1 is the frequency of jump from a nearest neighbor site to any one of the other possible p sites (third, fourth, or fifth nearest neighbors of the impurity). Figures illustrating these jumps may be found in reference 9.

^b The values of F_{jpa} listed here are those found in reference 9 for the case where a vacancy at a second nearest neighbor site from the impurity diffuses as if it were in a pure lattice. In general, $0 \leq F_{jpa} \leq 1$. In the face-centered cubic lattice, F_{jpa} always equals $\frac{1}{4}$ for the four w_1 jumps.

^c The $\cos\phi_p$ are geometric quantities which depend on the crystal lattice.

unity, the Nernst-Einstein relation [Eq. (1)] is not strictly obeyed when diffusion occurs by a vacancy mechanism.

3. DRIFT MOBILITY FOR AN INTERSTITIALCY MECHANISM

An equation similar to Eq. (12) can also be derived when diffusion occurs by an interstitialcy mechanism. In the elementary jump for this mechanism, an interstitial ion pushes a neighboring lattice ion into an interstitial site and moves into the lattice site itself. The motion of both ions participating in an interstitialcy jump will transport electric charge. Thus, to obtain the net change in electric potential energy resulting from such a jump, the displacement of both ions must be considered. For a collinear interstitialcy jump, where the two participating ions both move in the same direction,

$$\delta I_{oj} = -\frac{1}{2}(q_t + q_s)Ea \cos\phi_{oj}. \quad (13)$$

Here, δI_{oj} is the effective change in energy of motion for an interstitialcy jump which displaces a tracer ion in the j th direction, a is the ion jump distance (the distance between a lattice site and an adjacent interstitial site), q_t is the charge of the tracer, q_s is the charge of the solvent ion participating in the jump, and ϕ_{oj} is the angle between the electric field and the jump direction.

When diffusion occurs by a collinear interstitialcy mechanism, a tracer ion can jump from a lattice site to an adjacent interstitial site j only if an interstitial ion is present at site $-j$, the interstitial site on the side of the tracer opposite from site j . A flow of interstitialcies changes the probability that a new interstitialcy will approach a lattice ion from the $-j$ th direction. This changes the probability of occurrence of an uncorrelated tracer jump to interstitial site j by a factor G_{oj} . In the

Appendix, it is found for this mechanism:

$$G_{oj} = 1 + \frac{2q_s Ea}{kT} L \cos\phi_{oj}, \quad (14)$$

where L can be found from Eq. (A7) and Table I.

In the interstitialcy mechanism, half of the jumps are directed from a lattice site to an interstitial site and the other half from an interstitial site to a lattice site. As a result, only half of the jumps by any given ion are affected by the probability of an imperfection being at an adjacent site. For an interstitialcy mechanism, Eq. (6) thus becomes

$$\bar{v} = 2D^* a^{-1} [A + \frac{1}{2}B + \frac{1}{2}a(\partial \ln f / \partial x)]. \quad (15)$$

Here, A is given by Eq. (9) with δH_{oj} replaced by δI_{oj} , while B can be found from Eqs. (7) and (14). In a homogeneous crystal, f is independent of x . Thus, for an interstitialcy mechanism with collinear jumps, it follows that

$$\frac{\mu}{D^*} = \frac{q_s + q_t}{kT} \left\{ 1 + \frac{2q_s L}{q_s + q_t} \right\}. \quad (16)$$

The factor in braces in Eq. (16) arises because of the flow of interstitialcies which results from the presence of the electric field.

4. DISCUSSION

(a) Self-Diffusion

McCombie and Lidiard⁴ have shown that for self-diffusion by a vacancy mechanism,

$$\mu/D^* = (q_t/kT)(1/f), \quad (17)$$

and for self-diffusion by an interstitialcy mechanism

with collinear jumps,

$$\mu/D^* = (q_i/kT)(2/f). \quad (18)$$

These equations can be compared with Eqs. (12) and (16). For self-diffusion, q_i equals q_s . Thus, for self-diffusion by a vacancy mechanism, $(1+2L)$ should equal f^{-1} ; while, for self-diffusion by an interstitialcy mechanism, $(1+L)$ should equal f^{-1} . Values of L for self-diffusion (where $k_1=w_1$) can be found from the expressions in the last column of Table I. These values and previously calculated values^{7,8} of f satisfy the above relations. Since Eqs. (17) and (18) are exact equations, this shows that for self-diffusion Eqs. (12) and (16) are also exact.

(b) Impurity Diffusion

Monovalent Impurity in Monovalent Sublattice

For a monovalent impurity diffusing by a vacancy mechanism in a monovalent cation sublattice, $q_i = +e$ and $q_s = +e$, where e is the electronic charge. Then, Eq. (12) becomes

$$\mu/D^* = (e/kT)(1+2L). \quad (19)$$

Explicit expressions for L , calculated under the assumption that a vacancy which is not a nearest neighbor of an impurity diffuses as if it were in a pure lattice, are given in Table I in the Appendix. For a face-centered cubic sublattice, one finds

$$L = \frac{-2w_1 + 3k_1}{2w_1 + 5.15k_1}, \quad (20)$$

and

$$\frac{\mu}{D^*} = \frac{e}{kT} \frac{-2w_1 + 11.15k_1}{2w_1 + 5.15k_1}. \quad (21)$$

Equation (21) is very similar to Eq. (2), which was derived by a different method. The coefficients of k_1 in Eqs. (2) and (21) differ because a correction for the non-random return of vacancies which make k_1 jumps is included in Eq. (21) but not in Eq. (2). In general, the coefficient of k_1 in the denominator of Eq. (20) equals $7F$, where $F \leq 1$. Equation (2) corresponds to the case where $F = 1$.

For the case considered in Eq. (21),

$$f^{-1} = \frac{2w_2 + 2w_1 + 5.15k_1}{2w_1 + 5.15k_1}, \quad (22)$$

where w_2 is the rate of exchange of a vacancy with a neighboring impurity.⁹ Thus, $(1+2L)$ can differ appreciably from f^{-1} . This is true in general for impurity diffusion (in contrast to the result for self-diffusion).

⁷ K. Compaan and Y. Haven, *Trans. Faraday Soc.* **54**, 1498 (1958); **52**, 786 (1956).

⁸ A. H. Schoen and R. W. Lowen, *Bull. Am. Phys. Soc.* **5**, 280 (1960).

⁹ J. R. Manning, *Phys. Rev.* **116**, 819 (1959).

Divalent Impurity in a Monovalent Sub-lattice

As another example, the diffusion of a divalent impurity by a vacancy mechanism in a face-centered cubic sublattice of monovalent cations can be considered. In this case, $q_i = +2e$ and $q_s = +e$, so, from Eq. (12) one finds

$$\mu/D^* = (2e/kT)(1+L), \quad (23)$$

and, if L is given by Eq. (20), one obtains

$$\frac{\mu}{D^*} = \frac{2e}{kT} \frac{8.15k_1}{2w_1 + 5.15k_1}. \quad (24)$$

One must exercise care in applying Eqs. (23) and (24). These equations are valid if μ and D^* are measured in essentially homogeneous crystals (where all concentration gradients are negligible) and if the impurity does not appreciably affect the motion of a vacancy at a next nearest neighbor site. When $q_i \neq q_s$, these conditions frequently are not satisfied.

The analysis leading to Eq. (23) is valid only if the nonuniform concentration of divalent ions introduced to measure μ and D^* is small compared to the total vacancy concentration. When this condition is not satisfied, the vacancies which are introduced along with the divalent ions to preserve charge neutrality give rise to an appreciable gradient of vacancies. The electric field tends to sweep these vacancies toward one end of the specimen, but, at least to a certain extent, they are bound to the relatively immobile divalent ions. The effect this has on the vacancy flow is not clear. Also, as discussed by Lidiard,^{5,10} the probability of association of a vacancy and a divalent ion in a vacancy-impurity complex is a function of the divalent ion concentration. When there is an appreciable gradient of divalent ions, a factor depending on the derivative of the association probability must be introduced into Eq. (23). Both μ and D^* then will vary with position and time, so simultaneous values of these quantities will also be difficult to obtain experimentally.

These difficulties do not arise if the nonuniform concentration of divalent ions is small compared to the total vacancy concentration. This condition can be satisfied experimentally since radioactive tracer impurities with very high specific activity are available. A uniform vacancy concentration much greater than that introduced with the tracer impurities can be provided either by thermal vacancies or by vacancies resulting from a uniform concentration of non-tracer divalent ions.

Even when this condition for Eq. (23) is satisfied, Eq. (24) may not be completely valid. If the impurity ion differs significantly from the solvent ions, it can strongly influence the motion of a vacancy at a next nearest neighbor site. Then, the equations for L need to be modified. In the limit where the vacancy is so tightly

¹⁰ A. B. Lidiard, *Phil. Mag.* **46**, 815 (1955).

bound to the divalent ion that every k_1 jump is immediately followed by the return of the vacancy to a site neighboring on the tracer, μ/D^* goes to zero. In an intermediate case, where a vacancy at a next nearest neighbor site is weakly attracted to the divalent impurity, the coefficients of k_1 in Eqs. (20) and (24) will be somewhat decreased. Thus, Eq. (24) probably gives only an upper limit on μ/D^* .

(c) Diffusion Mechanism for Impurity Diffusion and Jump Frequencies Near an Impurity

The value of μ/D^* will be considerably larger for an impurity diffusing by an interstitialcy mechanism than by a vacancy mechanism. [See Eqs. (12) and (16).] Thus, as was pointed out by McCombie and Lidiard for self-diffusion,⁴ a measurement of μ/D^* could help to determine the diffusion mechanism.

Chemla¹¹ measured the values of μ and D^* for Cs diffusing in NaCl. He found $(\mu/D^*)(kT/e) \approx 0.9$ to 1.0 in the temperature range 575°C to 721°C. From Eq. (16) and the value of L ($=\frac{1}{2}$) given in Table I, it follows that for a monovalent cation impurity diffusing by an interstitialcy mechanism with collinear jumps in a face-centered cubic sublattice of monovalent cations (for example, the Na sublattice in NaCl),

$$\mu/D^* = 3e/kT. \quad (25)$$

Equation (25) predicts a value of μ/D^* three times as large as the measured value. Thus, one may conclude that Cs in NaCl does not diffuse to any great extent by an interstitialcy mechanism with collinear jumps. On the other hand, a value $\mu/D^* \approx e/kT$ is consistent with Eq. (21), which gives the value of μ/D^* for diffusion by a vacancy mechanism.

When the diffusion mechanism is known, relative values of the jump frequencies, such as w_1 and k_1 , can be estimated from the value of μ/D^* . From Eq. (21) and the experimental values of μ/D^* for Cs diffusing in NaCl, one can estimate that, if diffusion occurs by a vacancy mechanism, $w_1/k_1 \approx 1.5$ to 1.7 in the temperature range 721°C to 575°C. If the value of the correlation factor were known, one could also use Eq. (22) to determine the ratios w_2/k_1 and w_2/w_1 .

5. SUMMARY

A general expression [Eq. (12)] was derived, giving the value of μ/D^* when diffusion occurs by a vacancy mechanism in a homogeneous cubic crystal. The value of the quantity L which appears in this equation can be found from Eq. (A7) in the Appendix. Explicit expressions for L , calculated under the assumption that a vacancy which is not a nearest neighbor of an impurity diffuses as if it were in a pure lattice, are given in Table I. An expression for μ/D^* when diffusion occurs by an interstitialcy mechanism in a homogeneous cubic crystal is given in Eq. (16). These equations can help

¹¹ M. Chemla, Ann. phys. 1, 959 (1956).

determine the diffusion mechanism and the relative values of the jump frequencies near an impurity. The expressions for L include the effect of those dissociating vacancies which return to the impurity. Hence, for self-diffusion, Eqs. (12) and (16) reduce exactly to the proper expressions [Eqs. (17) and (18)]. The equations for μ/D^* apply best when the impurity has the same charge as the solvent ions in the sublattice of interest.

ACKNOWLEDGMENTS

The author wishes to thank Dr. A. B. Lidiard and Dr. R. E. Howard for their helpful comments.

APPENDIX—EFFECT OF AN ELECTRIC FIELD ON G_{oj} IN AN IONIC CRYSTAL

(a) Vacancy Mechanism

The solvent ion jump frequency w_{jp} for exchange of a vacancy on site j with an ion on site p is changed by an electric field so that

$$w_{jp} = w_{jpa}(1 + \epsilon \cos\phi_{jp}), \quad (A1)$$

where w_{jpa} is the value of w_{jp} in the absence of a field, ϕ_{jp} is the angle between the direction of the field and the line $j-p$, and ϵ is a small quantity. To first order,

$$\epsilon = -q_s E \lambda / 2kT, \quad (A2)$$

where q_s is the charge of the solvent ion, E the magnitude of the electric field, and λ the jump distance.

The effect of the electric field on the solvent ion jump frequencies causes a flow of vacancies. This flow changes the probability that a vacancy which has not previously exchanged with a given tracer ion will arrive at a site j next to the tracer. As a result, the probability of an uncorrelated tracer jump to site j is changed by a factor G_{oj} . If a vacancy at a next nearest neighbor site is not strongly bound to the tracer and the equilibrium vacancy concentration is constant throughout the crystal, it can be shown to a good approximation¹ that

$$G_{oj} = 1 - 2\epsilon \sum_{p=1}^{z-1} w_{jpa} \cos\phi_{jp} / \sum_{p=1}^{z-1} w_{jpa} F_{jpa}, \quad (A3)$$

Here, z is the number of nearest neighbors, and the summations are over $z-1$ sites neighboring on site j with the tracer site being excluded. Also, F_{jpa} is the fraction of vacancies making w_{jp} jumps which in the absence of an electric field effectively return to the tracer only from random directions. Values of $w_{jpa} F_{jpa}$ are listed in Table I.

One may define ϕ_p as the angle between the line $j-p$ and the line $o-j$ (see Fig. 1). Then, from the law of cosines for spherical triangles, one finds

$$\sum_{p=1}^{z-1} w_{jpa} \cos\phi_{jp} = \sum_{p=1}^{z-1} w_{jpa} \cos\phi_{oj} \cos\phi_p + \sum_{p=1}^{z-1} w_{jpa} \sin\phi_{oj} \sin\phi_p \cos\psi_p, \quad (A4)$$

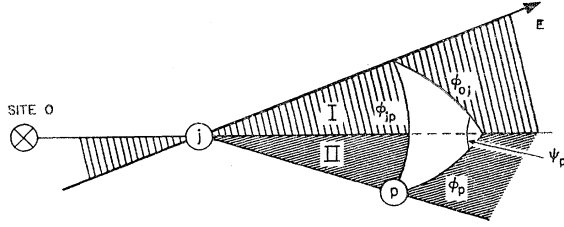


FIG. 1. Diagram showing the angles ϕ_{jp} , ϕ_{oj} , ϕ_p , and ψ_p . The tracer ion at site o is marked \times , and the direction of the electric field E is shown by the arrow. Site j is a nearest neighbor of the tracer. Site p is a nearest neighbor of site j .

where ψ_p is the angle between plane I, which is defined by the tracer, site j , and the direction of the electric field, and plane II, which is defined by the tracer, site j , and site p . If the line $o-j$ is an axis of twofold rotational symmetry, Eq. (A4) can be simplified. For every site p_1 for which $\sin\phi_{p_1} \neq 0$ there then will be another site p_2 such that $\sin\phi_{p_1} = \sin\phi_{p_2}$, $w_{jp_1a} = w_{jp_2a}$, and $\cos\psi_{p_1} = -\cos\psi_{p_2}$. Thus, the second sum on the right in Eq. (A4) equals zero. Similarly, if the line $o-j$ is an axis of threefold rotational symmetry, the sites for which $\sin\phi_p \neq 0$ can be divided into groups of three (p_1 , p_2 , and p_3) for which $\sin\phi_{p_1} = \sin\phi_{p_2} = \sin\phi_{p_3}$; $w_{jp_1a} = w_{jp_2a} = w_{jp_3a}$; and $\cos\psi_{p_1} + \cos\psi_{p_2} + \cos\psi_{p_3} = 0$; and again the second sum on the right in Eq. (A4) equals zero. Thus, whenever the line $o-j$ is an axis of two- or threefold rotational symmetry (a condition satisfied by all cubic lattices),

$$\sum_{p=1}^{z-1} w_{jp_a} \cos\phi_{jp} = \cos\phi_{oj} \sum_{p=1}^{z-1} w_{jp_a} \cos\phi_p. \quad (\text{A5})$$

Then, from Eqs. (A2) and (A3), one obtains

$$G_{oj} = 1 + (q_s E a / kT) L \cos\phi_{oj}, \quad (\text{A6})$$

where

$$L = \frac{\sum_{p=1}^{z-1} w_{jp_a} \cos\phi_p}{\sum_{p=1}^{z-1} w_{jp_a} F_{jp_a}}. \quad (\text{A7})$$

The quantity L depends only on the crystal geometry and the solvent jump frequencies w_{jp_a} in the absence of

an electric field. The entire dependence of G_{oj} on the direction of the electric field is contained in the term $\cos\phi_{oj}$.

Values of F_{jp_a} have been calculated for various cubic lattices under the assumption that a vacancy which is not a nearest neighbor of an impurity diffuses as if it were in a pure lattice.⁹ Values of $\cos\phi_p$ can be determined from the crystal geometry. The resulting values of $\sum w_{jp_a}$, $\sum w_{jp_a} F_{jp_a}$, $\sum w_{jp_a} \cos\phi_p$, and L for various cubic lattices are listed in Table I.

(b) Interstitialcy Mechanism

An analysis similar to that above will allow one to calculate G_{oj} when diffusion occurs by an interstitialcy mechanism. In a collinear jump, where both participating ions move in the same direction, the position of the excess electric charge moves twice as far as either of the two ions. Thus, a factor 2 must be introduced into Eq. (A2), and one finds

$$G_{oj} = 1 + (2q_s E a / kT) L \cos\phi_{oj}. \quad (\text{A8})$$

Here, a is the ion jump distance (from a lattice site to an adjacent interstitial site), and L is given by Eq. (A7) with w_{jp_a} in this case being the frequency in the absence of an electric field with which an ion at interstitial site j (adjacent to the tracer ion at lattice site o) will jump from this site by cooperating in an interstitialcy jump with a non-tracer neighbor at lattice site p . In the interstitialcy mechanism, the imperfections (interstitialcies) move in the same direction as do the ions, while in the vacancy mechanism the imperfections (vacancies) move in the opposite direction. However, a flow of ions in the $+j$ th direction leads in both cases to a G_{oj} term that increases the probability of a tracer jump in the $+j$ th direction.

In Table I, values of L for an interstitialcy mechanism with collinear jumps are given for two common lattices. Here again the values of F_{jp_a} are those found in reference 9. Values of F_{jp_a} for other cubic lattices can be calculated by the method outlined in reference 9, and values of L for these cases then can be obtained from Eq. (A7).