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Diffusion in a Chemical Concentration Gradient

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The concept of correlated reverse jumps is used to treat correlation effects in a chemical concentration gradient. It is shown that the correlation factor associated with a given atom jump will be very nearly the same as that in a homogeneous alloy having the composition associated with the point midway between the initial and final atom positions for that jump. This is true for either a vacancy or interstitialcy mechanism. With the aid of this result, expressions for the atom flux of a given species and the mean atom displacement of a layer of diffusing atoms are derived from a purely atomistic approach, taking correlation effects into account. These expressions differ from equations obtained by Darken and LeClaire in that they contain extra terms which arise where there is a flow of vacancies or interstitialcies. These extra terms can appreciably increase the predicted Kirkendall shift. They appear as both diagonal *and* cross terms in the general thermodynamic formulation of the diffusion equations. The method used here to analyze the effect of a chemical concentration gradient can also be used to study the effect of other types of gradients and external driving forces.

1. INTRODUCTION

IN the present paper, diffusion in a chemical concentration gradient in crystalline solids is considered from an atomistic viewpoint. Correlation effects and the effect of a flow of imperfections are treated explicitly. General expressions are found relating the atom flux and mean drift velocity to the magnitude of the driving force, i.e., the effect that the gradient has on the atom jump frequencies. These expressions differ from those found by Darken[1] and LeClaire[2] in that they contain additional terms arising from the flow of imperfections. Also, the correlation factor appears explicitly and in a somewhat different manner than is indicated by LeClaire.[2] The additional term from the flow of imperfections increases the predicted Kirkendall shift by an appreciable amount and, to a smaller extent, increases the predicted chemical interdiffusion coefficient.

An effect from a flow of imperfections is physically reasonable. When diffusion occurs by a vacancy mechanism, a given atom cannot jump until a vacancy has moved into a neighboring site. If the flow of vacancies is from right to left (see Fig. 1), a vacancy is more likely to approach a given atom from the right, cause a jump, and then move away to the left than it is to approach from the left, cause a jump, and then move away to the right. As a result, the atom will jump more frequently to the right than to the left. This effect depends on the frequency with which vacancies approach a given atom. Thus, it depends on the jump frequencies of atoms *other* than the given atom. Similar reasoning applies when there is a flow of interstitialcies.

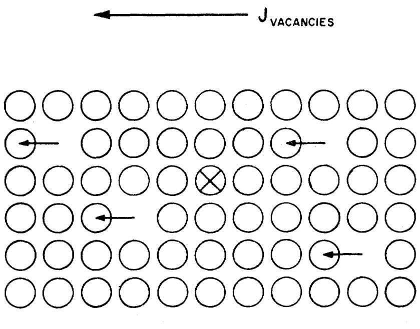

FIG. 1. Effect of a flow of vacancies. The tracer atom is marked ×. When the vacancy flow is from right to left as shown in the figure, the individual vacancies are more likely to approach the tracer from the right than from the left.

Diffusion in a chemical concentration gradient by a vacancy mechanism will be considered explicitly. The method which is used is quite general, however, and can be applied to diffusion in other types of gradients or by an interstitialcy mechanism. Attention will be centered on cubic crystals, since this allows a much simpler treatment.

In certain respects, the present method is similar to that used by Lidiard[3] to treat diffusion in an electric potential gradient. In the present method, however, the motion of a given (tracer) atom is followed. This allows one to distinguish between vacancy flow effects, which arise from the preferred direction of motion of atoms other than the tracer, and Bardeen-Herring correlation effects,[4] which arise from the effect that the motion of the tracer atom itself has on the local vacancy distribution. Also, it allows a more detailed treatment of correlation effects and a purely atomistic calculation of the mean atom drift velocity.

2. CORRELATION EFFECTS

When diffusion occurs by a vacancy mechanism, the elementary atom jump consists of an atom exchanging places with a neighboring vacancy, i.e., the atom

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[1] L. S. Darken, Trans. Am. Inst. Mining Met. Engrs. **175**, 184 (1948).

[2] A. D. LeClaire, Phil. Mag. **3**, 921 (1958).

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

[4] J. Bardeen and C. Herring, in *Atom Movements* (American Society for Metals, Cleveland, Ohio, 1951), p. 87; also in *Imperfections in Nearly Perfect Crystals*, edited by W. Shockley, J. H. Holloman, R. Maurer, and E. Seitz (John Wiley & Sons, Inc., New York, 1952), p. 261.

jumping into a neighboring vacant lattice site. After such a jump, the vacancy is at the site which was previously occupied by the atom. As a result, the atom on its next jump has a greater than random probability of returning to its original site, and there is a correlation between the directions of successive jumps taken by a given atom.[4]

The atom flux J of a tracer impurity for planar diffusion in the x direction in the absence of a driving force can be expressed as

$$J=-D^*(\partial c/\partial x), \tag{1}$$

where c is the concentration of the tracer and D^* is the diffusion coefficient. In the absence of correlation, random walk theory predicts that in cubic crystals

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

where λ is the jump distance and ν is the jump frequency for the atoms in question. In the absence of a driving force, correlation effects can be taken into account by introducing a correlation factor f_c on the right-hand side of Eq. (2). In cubic crystals,[4–6]

$$f_c=\lim_{n\to\infty}\left[\frac{\langle x^2\rangle_{\mathrm{av}}}{\frac{1}{3}n\lambda^2}\right], \tag{3}$$

where $\langle x^2\rangle_{\mathrm{av}}$ is the mean-square atom displacement in the x direction after n jumps per atom. For diffusion by a vacancy mechanism in a pure cubic crystal,[5,6]

$$f_c=\frac{1+\langle\cos\theta\rangle_{\mathrm{av}}}{1-\langle\cos\theta\rangle_{\mathrm{av}}}, \tag{4}$$

where θ is the angle between the directions of two successive jumps by the same atom, and the average of $\cos\theta$ is taken over all successive pairs of atom jumps.

The above method of correcting for correlation serves quite well when there is no driving force tending to make the atoms jump more frequently in one direction than another. However, when a driving force is present, several difficulties arise. For example, the mean atom displacement in the x direction, $\bar{x}$, is proportional to n, and for large values of n,[2]

$$\langle x^2\rangle_{\mathrm{av}}\approx\tfrac{1}{3}n\lambda^2+(\bar{x})^2. \tag{5}$$

Therefore, $\langle x^2\rangle_{\mathrm{av}}$ contains a contribution proportional to n^2; and in general the limit in Eq. (3) will not exist. In addition, if one wishes to relate the value of $\bar{x}$ to the activation energies for jumps in the $+x$ and $-x$ directions, one must take correlation effects into account. This cannot be done merely by using Eq. (3).

To avoid these difficulties, a different approach is used in the present paper. Effective jump frequencies are calculated by considering successive exchanges of an atom with a given vacancy. The atom flux and mean atom drift velocity then are calculated from these frequencies. This approach allows a calculation of correlation effects in the presence of a driving force and gives the same result in the absence of a driving force as does the more conventional approach using Eq. (3).

This general approach has been used by previous investigators to obtain approximate expressions for the correlation factor in homogeneous crystals.[4,7] Since effects from vacancies which diffuse away through the lattice and subsequently return were not treated, these expressions were not exact. In the present paper, however, these effects are considered; so, for diffusion in pure cubic crystals, the present treatment is exact. The manner in which vacancies return will be affected by the presence of a gradient; but, to a large extent, this can be taken into account, so the resulting expressions also are good approximations for diffusion in a gradient in cubic crystals.

The situation in an alloy is more complicated than in a pure crystal, since local fluctuations in composition can occur. Even in a homogeneous alloy, the motion of a vacancy rearranges the atoms in the vicinity of the vacancy. This gives rise to a correlation between the directions of successive jumps by a given vacancy. In the present paper, effects arising from any such fluctuations or rearrangement of solvent atoms near a vacancy are neglected. However, to a large extent, these effects average out, so no great error should be introduced by this procedure. To illustrate the method, diffusion in the absence of a gradient is treated first. Then, modifications that are necessary when a gradient is present are considered.

3. METHOD OF CORRELATED JUMPS

A. Correlated Reverse Jumps

When diffusion occurs by a vacancy mechanism, the basic diffusion process may be described as follows: First, a *new* vacancy which has not previously exchanged with a given tracer atom arrives at one of the sites neighboring on this atom. Then, the vacancy may exchange places with the atom, perhaps many times; and finally the vacancy moves permanently away from the atom. The first exchange of an atom with a given vacancy causes the atom to be displaced in a certain direction. In the following discussion, this direction will be called the *forward* direction, and any atom jump in this direction will be called a forward jump. Each new vacancy which exchanges with a given atom defines its own forward direction. After an original forward jump has occurred, the vacancy is in the proper position to allow the atom to make a reverse jump, back to its original position. Such a reverse jump, caused by the same vacancy, will be called a *correlated reverse jump*. This is most likely to occur on

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[5] A. D. LeClaire and A. B. Lidiard, Phil. Mag. **1**, 518 (1956).

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

[7] A. H. Schoen, Convair Research Note No. 22, July, 1958 (unpublished).

the first jump of the vacancy following the forward jump. However, even if the vacancy moves off through the lattice and does not immediately re-exchange places with the atom, it still may eventually return and do so. These delayed exchanges also give rise to correlated reverse jumps.

Those vacancies which return and re-exchange with the atom from a direction such that $\cos\psi \neq -1$, where ψ is the angle between the directions of two successive tracer jumps caused by the same vacancy, obviously do not cause reverse jumps in the strict sense. However, in pure cubic crystals, the net tracer displacement resulting from these vacancies is exactly the same as if a certain fraction returned to the site corresponding to $\cos\psi = -1$ alone, or in fact never left this site.[8] This conclusion also is valid for diffusion in homogeneous alloys if effects from fluctuations in local composition are eliminated by averaging over many tracer atoms. As a result, a vacancy at a site neighboring on a tracer can be regarded as having an effective probability P of exchanging with the tracer and an effective probability $(1-P)$ of permanently moving away or randomizing its position around the tracer. The actual three-dimensional correlation problem in these crystals then reduces to an equivalent one-dimensional problem involving jumps with $\cos\psi = -1$ alone, but with tracer-vacancy exchanges occurring with probability P.

In accordance with the above discussion, the effective probability P_{oj} of occurrence of a correlated reverse jump after an atom jump from site j to site o is given by[9]

$$P_{oj} = w_{Tjo}/(w_{\beta jo} + w_{Tjo}), \tag{6}$$

where w_{Tjo} is the jump frequency for exchange of a vacancy on site j with a tracer on site o, and $w_{\beta jo}$ is the effective frequency with which the vacancy on site j will exchange with some other atom. The effect of the returning vacancies is included in Eq. (6) by specifying that jumps which are followed by an effective return of the vacancy to site j will not contribute to $w_{\beta jo}$. Thus, $w_{\beta jo}$ is given by

$$w_{\beta jo} = \sum_{p=1}^{z-1} w_{jp}(1 - Y_{jpa} - Y_{jpe}), \tag{7}$$

where w_{jp} is the frequency with which a vacancy which is on site j will jump to a neighboring site p, Y_{jpa} is the fraction of such jumps which are followed an actual return of the vacancy to site j, Y_{jpe} is the fraction of such jumps which are effectively cancelled by the return of the vacancy to nearest neighbor sites other than j, and z is the number of nearest neighbors. The summation is over only $z-1$ sites neighboring on site j, since exchanges of the vacancy with the tracer are excluded from the sum. When $w_{\beta jo}$ is defined in this manner, P_{oj} in the absence of a gradient[8] will equal $\langle -\cos\theta \rangle_{\text{av}}$. Values of $w_{\beta jo}$ for various cubic lattices in the absence of a gradient have been calculated in reference 8 for the case where a vacancy jump originating at a next-nearest site from the tracer is not affected by the presence of the tracer. These values and the corresponding values of $\sum w_{jp}$ are given in Table I.

B. Effective Jump Frequency

When an atom and vacancy undergo a series of exchanges with $\cos\psi$ being -1 for each pair of successive exchanges, the atom will merely jump back and forth along the line determined by the original jump (see Fig. 2). Since each correlated reverse jump in such a series merely cancels the effect of the forward jump preceding it, neither the reverse jumps nor the preceding forward jumps are effective in causing random walk diffusion. The *effective jump frequency* ν_{oje} for atom jumps from site o to site j will be defined as the frequency which would result in the same average atom displacement along the line o-j as that resulting from the sequences of correlated jumps which actually occur. Thus,

$$\lambda \nu_{oje} = U_{oj} \Omega_{oj}, \tag{8}$$

where U_{oj} is the average atom displacement resulting from a series of jumps which starts with the atom on site o and the vacancy on site j, and Ω_{oj} is the frequency with which a tracer atom on site o makes an original forward jump by exchanging with a new vacancy on

TABLE I. Jump frequencies in the absence of a gradient.[a]

Lattice	$\sum_{p=1}^{z-1} w_{jp}$	$w_\beta = \sum_{p=1}^{z-1} w_{jp} F_{jp}$
	Vacancy mechanism	
Face-centered cubic	$4w_1 + 7k_1$	$2w_1 + 5.15k_1$
Body-centered cubic	$3w_1 + 4k_1$	$2.35w_1 + 2.98k_1$
Simple cubic	$4w_1 + k_1$	$3.04w_1 + 0.73k_1$
Diamond	$3w_1$	$2w_1$
	Interstitialcy mechanism (with collinear jumps)	
AgCl	$3w_1$	$2w_1$
Face-centered cubic	$4w_1 + k_1$	$3.26w_1 + 0.74k_1$

[a] Values of w_{jp} 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 (non-dissociative 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 jumps). For 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 jumps 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 8. The values of w_β are those found in reference 8 for the case where a vacancy jump from a second-nearest neighbor site is not affected by the presence of the impurity.

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[8] J. R. Manning, Phys. Rev. **116**, 819 (1959).

[9] The symbol w will refer to a vacancy jump frequency, while ν will refer to an atom jump frequency. When subscripts are used to designate the two sites involved in a jump, the one referring to the position of the *atom* before the jump will normally appear first, i.e., P_{oj}, ν_{oje}. However, in designating *vacancy* jump frequencies, the subscript giving the *vacancy* position before the jump will precede that giving the vacancy position after the jump, i.e., w_{Tjo}, w_{jp}.

neighboring site j. For a series of correlated jumps,

$$U_{oj}=\lambda(1-P_{jo}+P_{jo}P_{oj}-P_{jo}^{2}P_{oj}+\cdots),\tag{9}$$

where P_{jo} is the probability of occurrence of a correlated reverse jump after an atom jump from site o to site j and is defined by an equation analogous to Eq. (6) for P_{oj}. The second term in parentheses in Eq. (9) arises from the effective probability of occurrence of a correlated reverse jump following an original forward jump (Fig. 2b), the third term from the effective probability of a second forward jump in a sequence of forward and correlated reverse jumps (Fig. 2c), and so on. Also,

$$\Omega_{oj}=\nu_{\alpha jo}w_{Tjo}/(w_{\beta jo}+w_{Tjo}),\tag{10}$$

where $\nu_{\alpha jo}$ is the effective frequency with which new vacancies first arrive at site j, and $w_{\beta jo}$ and w_{Tjo} are defined above. Since those vacancies which effectively return to one of the sites neighboring on the tracer after having previously been at such a site are treated as not contributing to $w_{\beta jo}$, one must specify that these vacancies do not contribute to $\nu_{\alpha jo}$ either. Thus,

$$\nu_{\alpha jo}=\sum_{p=1}^{z-1}N_{vp}w_{pj}(1-Y_{pja}-Y_{pje}),\tag{11}$$

where N_{vp} is the molar concentration of vacancies at site p, w_{pj} is the frequency with which a vacancy which is on site p will jump to site j, Y_{pja} is the fraction of such jumps which involve the return of a vacancy which has previously been on site j and hence do not contribute to $\nu_{\alpha jo}$, and Y_{pje} is the fraction of w_{pj} jumps which involve the effective return of a vacancy which has been on one of the sites *other* than site j neighboring on the tracer. From Eqs. (8)–(10), it follows that

$$\nu_{oje}=w_{Tjo}\frac{\nu_{\alpha jo}}{w_{\beta jo}}\left(\frac{w_{\beta jo}}{w_{\beta jo}+w_{Tjo}}\right)\frac{1-P_{jo}}{1-P_{jo}P_{oj}},\tag{12}$$

and one finds from Eq. (6)

$$1-P_{oj}=w_{\beta jo}/(w_{\beta jo}+w_{Tjo}).\tag{13}$$

A basic jump frequency ν_{ojb} for an atom jump from site o to site j can be defined such that

$$\nu_{ojb}=N_{vjJ}w_{Tjo},\tag{14}$$

where N_{vjJ} is the equilibrium probability that a vacancy would be present at a given neighboring site j if the tracer were in a homogeneous alloy having the composition associated with this site. Equation (12) then can be rewritten as

$$\nu_{oje}=\nu_{ojb}G_{oj}f_{oj},\tag{15}$$

where

$$G_{oj}=\nu_{\alpha jo}/N_{vjJ}w_{\beta jo},\tag{16}$$

and

$$f_{oj}=(1-P_{jo})(1-P_{oj})/(1-P_{jo}P_{oj}).\tag{17}$$

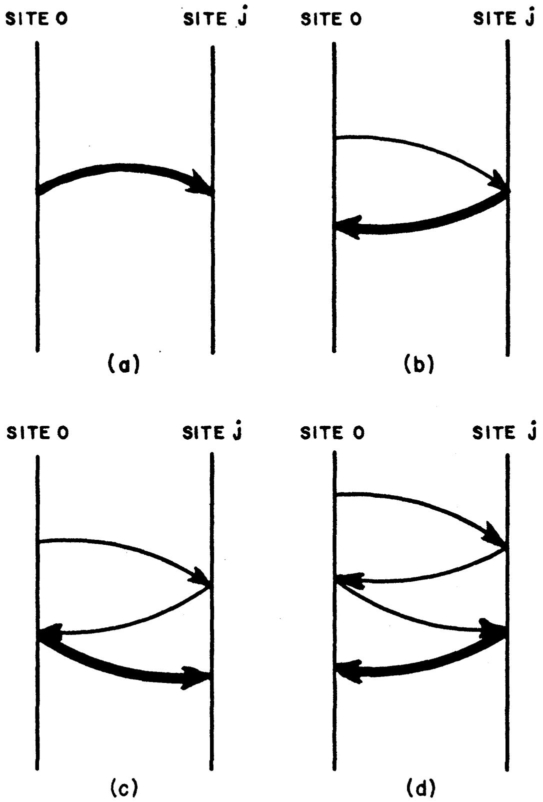

FIG. 2. Contributions to the effective atom jump frequency ν_{oje}. The arrows show jumps made by an atom originally on site o. Further jumps may occur in each sequence. The jumps shown in boldface give the first four terms in Eq. (9). The vertical displacement of the jumps is not real and is shown only to increase legibility.

Equation (15) is a particularly convenient expression for ν_{oje} since ν_{ojb}, G_{oj}, and f_{oj} can be given useful physical interpretations. For example, ν_{ojb} through its dependence on N_{vjJ} is directly related to the energy of formation for a vacancy in a homogeneous alloy and through its dependence on w_{Tjo} to the energy of motion for an atom jump from site o to site j. Also, G_{oj} can be identified as a factor which arises from the effect of a flow of vacancies, and f_{oj} as the factor which arises because a vacancy can exchange more than once with a given atom. As a result, f_{oj} can be identified as the correlation factor.

C. In the Absence of a Gradient

In the absence of a gradient, there will be no net flow of vacancies between sites j and p so, in this case,

$$N_{vj}w_{jp}=N_{vp}w_{pj},\tag{18}$$

where N_{vj} is the molar concentration of vacancies at site j. Also, the number of vacancy jumps from site j to site p which effectively are cancelled by the subsequent return of the vacancy to site j must equal the number of vacancy jumps from site p to site j which effectively cancel (and are cancelled by) previous j to

p jumps, so

$$N_{vj}w_{jp}Y_{jpa}=N_{vp}w_{pj}Y_{pja}. \tag{19}$$

Similarly,

$$N_{vj}w_{jp}Y_{jpe}=N_{vp}w_{pj}Y_{pje}. \tag{20}$$

If the over-all vacancy concentration is maintained at its equilibrium value,

$$N_{vj}=N_{vjJ} \tag{21}$$

in the absence of a gradient. Upon substitution of Eqs. (18)–(21) into Eqs. (7), (11), and (16), one finds that G_{oj} in the absence of a gradient equals unity.

When there is no gradient, the jump frequencies w_{Tjo} and $w_{\beta jo}$ will be independent of direction and position. Thus, the subscripts o and j can be omitted, and $P_{oj}=P_{jo}=P$, where $P=w_T/(w_\beta+w_T)$. Equations (15) and (17) then reduce to

$$\nu_e=f\nu_b, \tag{22}$$

with

$$f=(1-P)/(1+P). \tag{23}$$

As discussed earlier, w_β does not include any contribution from those vacancies which effectively return to the same site after making a w_{jp} jump. Thus, $P=\langle-\cos\theta\rangle_{\text{av}}$; and it follows from Eqs. (4) and (23) that

$$f=f_c, \tag{24}$$

where f_c is the correlation factor which is obtained when $\langle x^2\rangle_{\text{av}}$ is evaluated directly.

In the absence of a gradient, correlations between the directions of successive atom jumps arise solely because a given vacancy may exchange with the same atom more than once. This has been taken fully into account in the calculation of the effective jump frequency. The factor $(1-P_{jo})/(1-P_{jo}P_{oj})$ in Eq. (12) takes into account the possibility that a given jump may be *followed* by a series of correlated exchanges of the atom with the same vacancy, while the factor $(1-P_{oj})$ from Eq. (13) takes into account the possibility that a given jump may have been *preceded* by an exchange of the atom with the given vacancy. Hence, the jump frequency in Eq. (2) can be treated as an effective jump frequency; and

$$D^*=\tfrac{1}{6}\lambda^2\nu_e=\tfrac{1}{6}\lambda^2\nu_b f, \tag{25}$$

where ν_e is an effective jump frequency and ν_b a basic jump frequency. The right-hand expression is the usual correlated walk expression for the diffusion coefficient D^*.

D. f_{0j} in a Gradient

A chemical concentration gradient can affect the vacancy jump frequencies both because of chemical potential effects in a non-ideal solid solution and because the energy of motion may be a function of composition.[2] If w_{TO} is the frequency with which a vacancy in a homogeneous alloy having the composition associated with site o would exchange with a neighboring tracer atom, the value of w_{Tjo} in a gradient is given by[10]

$$w_{Tjo}=w_{TO}+\sigma, \tag{26}$$

where σ is a small quantity depending on the magnitude and direction of the gradient. The gradient also can affect the manner in which vacancies which make j-p jumps will return to the tracer. However, to a good approximation. Eq. (6) will still be valid with

$$w_{\beta jo}=w_{\beta O}+\rho, \tag{27}$$

where $w_{\beta O}$ is the value of w_β in a homogeneous crystal having the composition associated with site o and ρ is a small quantity. The nature of this approximation is discussed in more detail in the Appendix. Even in the presence of a gradient, the average tracer displacement then is given by Eq. (9); and Eqs. (15)–(17) follow as before.

When Eqs. (26) and (27) are substituted into Eq. (6), one finds

$$P_{oj}=(w_{TO}+\sigma)/(w_{\beta O}+w_{TO}+\rho+\sigma). \tag{28}$$

Similarly, if w_{TJ} and $w_{\beta J}$ are the values of w_T and w_β in a homogeneous alloy having the composition associated with site j,

$$P_{jo}=(w_{TJ}-\sigma)/(w_{\beta J}+w_{TJ}-\rho-\sigma). \tag{29}$$

Since the o-j jumps are just the reverse of the j-o jumps, the small quantities σ and ρ in Eq. (29) will be the same to first order as those in Eqs. (26)–(28). The effective probability of return P_O in a homogeneous alloy having the composition associated with site o is given by

$$P_O=w_{TO}/(w_{\beta O}+w_{TO}), \tag{30}$$

while that in a homogeneous alloy having the composition with site j is given by

$$P_J=w_{TJ}/(w_{\beta J}+w_{TJ}). \tag{31}$$

When these relations are substituted in Eq. (17), one finds to first order in small quantities,

$$f_{oj}=\frac{(1-P_J)(1-P_O)}{1-P_JP_O}=\frac{(1-P_{J/2})^2}{1-(P_{J/2})^2}=\frac{1-P_{J/2}}{1+P_{J/2}}, \tag{32}$$

where $P_{J/2}$ is the effective probability of occurrence of a return jump in a homogeneous alloy having the composition associated with the point midway between sites o and j. Also, $P_{J/2}$ is equal to the value of

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[10] When lower-case subscripts refer to sites in the crystal, the corresponding capital letter subscripts refer either to the plane containing the site or to a homogeneous alloy having the composition associated with the site. Macroscopically the composition can be considered to vary continuously as a function of position. The composition associated with a given site is the value of the macroscopic composition at the point of the site.

$\langle -\cos\theta\rangle_{\mathrm{av}}$ in this alloy, so it follows from Eqs. (4) and (32) that

$$f_{oj}=f_{J/2}, \tag{33}$$

where $f_{J/2}$ is the correlation factor in a homogeneous alloy having the composition associated with the midpoint between sites o and j. In Eq. (17), f_{oj} depends in the same manner on the probability P_{oj} of jumps from site o to site j as on the probability P_{jo} of jumps from site j to o. Thus, it is reasonable that f_{oj} depends on the composition associated with the point midway between sites o and j.

4. PHYSICALLY MEASURABLE QUANTITIES

A. Atom Flux

A procedure very similar to that followed by Lidiard[3] can be used to calculate the atom flux from the effective jump frequencies. When diffusion occurs by a vacancy mechanism in a cubic lattice, an atom can move from one side of a given (100) plane to the other side only by passing through a lattice site in this plane. Thus, the atom flux equals the number of lattice sites per unit area multiplied by the net number of atoms per unit time passing through a given site. The number of lattice sites per unit area equals the number n of lattice sites per unit volume multiplied by the distance a between neighboring (100) planes. The net number of atoms passing through a given site can be found by enumerating the number of atoms entering and leaving this site in the positive and negative x directions, and then counting each as contributing half an atom to the flux. Thus, for a given species, the flux J_o in the positive x direction at the plane containing site o is given by

$$J_o=\tfrac{1}{2}na\{N_O(Z_+\nu_{O+e}-Z_-\nu_{O-e}) +N_-Z_-\nu_{-Oe}-N_+Z_+\nu_{+Oe}\}, \tag{34}$$

where the subscripts O, $+$, and $-$ refer respectively to plane O, which contains site o, and to the neighboring planes in the positive and negative x directions; N_H in general is the mole fraction of atoms of the given species on plane H; Z_H is the number of sites on plane H which neighbor on site o; and ν_{HGe} is the effective jump frequency for a jump from a site on plane H to a site on plane G. Effective jump frequencies appear in Eq. (34) instead of basic jump frequencies, since forward jump-correlated reverse jump pairs of jumps do not contribute to the net diffusive flow of atoms.

For all sites j on plane $+$, $\cos\phi_{oj}=a/\lambda$, where ϕ_{oj} is the angle between the x direction and the line o-j connecting site o to site j, and λ is the distance between site o and site j. Similarly, $\cos\phi_{oj}=0$ for sites on plane O; and $\cos\phi_{oj}=-a/\lambda$ for sites on plane $-$. By definition, $c_H=nN_H$, where c_H is the number of atoms of the given species per unit volume in a region centered at plane H. Thus, Eq. (34) can be rewritten as

$$J_o=\tfrac{1}{2}\lambda\Big[c_o\sum_{j=1}^{z}\nu_{oje}\cos\phi_{oj}-\sum_{j=1}^{z}c_j\nu_{joe}\cos\phi_{oj}\Big], \tag{35}$$

where c_o and c_j are the concentrations of the given species at the planes containing sites o and j; and ν_{oje} and ν_{joe} are the effective jump frequencies from site o to site j and from site j to site o, respectively. The quantity ν_{oje} can be evaluated from Eq. (15) and a detailed consideration of f_{oj}, ν_{ojb}, and G_{oj}; while ν_{joe} can be evaluated from Eq. (15) and the equation

$$\nu_{joe}=\nu_{o-je}[1+\lambda\cos\phi_{oj}(\partial\ln\nu_e/\partial x)], \tag{36}$$

where site $-j$ is the site on the opposite side of site o from site j.

The factor f_{oj} has been considered in the previous section. From Eq. (33), it follows to first order in small quantities that

$$f_{oj}=f_o[1+\tfrac{1}{2}\lambda\cos\phi_{oj}(\partial\ln f/\partial x)], \tag{37}$$

where f_o is the correlation factor in a homogeneous alloy having the composition associated with site o. In Eq. (14) defining ν_{ojb}, the quantity N_{vjJ} is directly related to the energy of formation for a vacancy, while w_{Tjo} is directly related to the energy of motion for an atom jump. A gradient or driving force in the x direction will change these by an amount proportional to $\cos\phi_{oj}$, so to first order in small quantities,

$$\nu_{ojb}=\nu_{ob}(1+A\cos\phi_{oj}), \tag{38}$$

where ν_{ob} is the basic jump frequency for a jump between two sites in a homogeneous alloy having the composition associated with site o, and A is a small quantity depending on the chemical concentration gradient or other driving force but not depending on j. Finally, in Eq. (16), the jumps which contribute to $\nu_{\alpha jo}$ and $w_{\beta jo}$ are just the reverse of one another. When there is a driving force along the x axis, the energies of motion and formation, and hence the jump frequencies, for these jumps will be changed by an amount proportional to $\cos\phi_{oj}$. Thus to first order in small quantities,

$$G_{oj}=1+B\cos\phi_{oj}, \tag{39}$$

where B is a small quantity depending on the gradient or driving force but not depending on j. This is discussed more fully in the Appendix.

When Eqs. (37)–(39) are substituted in Eq. (15), one finds to first order in small quantities,

$$\nu_{oje}=f_o\nu_{ob}\{1+\cos\phi_{oj}[A+B+\tfrac{1}{2}\lambda(\partial\ln f/\partial x)]\}, \tag{40}$$

and

$$\nu_{o-je}=f_o\nu_{ob}\{1-\cos\phi_{oj}[A+B+\tfrac{1}{2}\lambda(\partial\ln f/\partial x)]\}. \tag{41}$$

In addition,

$$c_j=c_o[1+\lambda\cos\phi_{oj}(\partial\ln c/\partial x)], \tag{42}$$

while, in all cubic lattices, for m an odd integer,

$$\sum_{j=1}^{z} \cos^m \phi_{oj} = 0, \tag{43}$$

and

$$\sum_{j=1}^{z} \cos^2 \phi_{oj} = \tfrac{1}{3} z. \tag{44}$$

When Eqs. (40)–(44) are substituted into Eq. (35) and the subscripts o are omitted, one finds

$$J = 2cD^* \lambda^{-1}(A+B) - D^*(\partial c/\partial x) - cD^*(\partial \ln\nu/\partial x), \tag{45}$$

where

$$\nu = z\nu_b = zf^{-1}\nu_e, \tag{46}$$

and

$$D^* = \tfrac{1}{6}\lambda^2 \nu f. \tag{47}$$

Explicit values of A and B can be obtained by evaluating Eqs. (14) and (16). LeClaire[2] has considered the effect that a chemical concentration gradient can have on the quantities appearing in Eq. (14). If vacancies are in local equilibrium, his analysis shows

$$A = \tfrac{1}{2}\lambda[(\partial \ln\nu/\partial x) - (\partial \ln\gamma/\partial x)], \tag{48}$$

where γ is the activity coefficient of the diffusing species. When Eq. (48) is substituted into Eq. (45), one finds

$$J_i = 2c_i D_i^* \lambda^{-1} B - D_i^*[1 + (\partial \ln\gamma_i/\partial \ln N_i)](\partial c_i/\partial x), \tag{49}$$

where the subscript i refers to the component under consideration. The term $-D_i^*[1+(\partial \ln\gamma_i/\partial \ln N_i)] \times (\partial c_i/\partial x)$ is the term which appears in the usual Darken equation.[1] The term involving B is an additional term which gives the effect of a flow of vacancies. This additional term can appreciably affect the predicted Kirkendall shift. Also, to a lesser extent, it will alter the predicted chemical interdiffusion coefficients.

B. *B* Term—Vacancy Flow Term

When a gradient causes a vacancy flow, vacancies will approach an atom more frequently from one direction than another. This will not affect the factors f_{oj} and ν_{ojb} in Eq. (15) since f_{oj} depends equally on the probabilities of jump in the $+j$th and $-j$th directions and ν_{ojb} depends on what happens after a vacancy arrives at a site neighboring on the tracer. Therefore, the total effect of the flow of vacancies must be contained in the factor G_{oj} in Eq. (15) and in the term involving B in Eq. (45). To first order in small quantities, B will be proportional to the difference between the vacancy jump frequencies with and against the vacancy flow. Hence, B will be proportional to the magnitude of the vacancy flow.

It is shown in the Appendix that for diffusion in a face-centered cubic binary alloy containing species q and r,

$$B \approx \frac{\lambda(w_q - w_r)}{7.15w}\left(1 + \frac{\partial \ln\gamma_i}{\partial \ln N_i}\right)\frac{\partial N_r}{\partial x}, \tag{50}$$

where w_q and w_r are the jump frequencies for exchange of a vacancy with a given neighboring q or r atom in a homogeneous alloy having the composition associated with site o; w is the average vacancy jump frequency in such an alloy, equal to $N_q w_q + N_r w_r$; and N_q and N_r are the mole fractions of q and r type atoms at site o. [Equation (50) for B differs only slightly from the similar equation for the quantity $-\Delta F/2kT$ found in a previous paper.[11]] It then follows from Eqs. (49) and (50) that

$$J_i \approx -D_i^*\left(1 + \frac{\partial \ln\gamma_i}{\partial \ln N_i}\right)\left\{\frac{\partial c_i}{\partial x} - \frac{2N_i(w_q - w_r)}{7.15w}\frac{\partial c_r}{\partial x}\right\}. \tag{51}$$

Approximate expressions for B and J_i in other cubic lattices can be obtained by replacing the quantity $7.15w$ in Eqs. (50) and (51) by the value of w_β in these other lattices as given in Table I with all w_{jp} set equal to the average vacancy jump frequency w.

C. Kirkendall Shift

The quantity B in Eq. (50) is not negligible. In fact, it is large enough to affect the Kirkendall shift appreciably. This will be discussed in the present section.

If a given lattice plane in a crystal containing a chemical concentration gradient is marked by inserting inert wires or foils at this plane and diffusion is allowed to occur, it is found that the markers frequently move toward one end of the specimen.[12] This shift in position of the markers relative to the ends of the specimen is called the Kirkendall shift and arises when there is a net flow of atoms across the plane defined by the markers. If there is no change in the dimensions of the specimen normal to the gradient, the velocity v of the markers in a binary alloy is given by[1]

$$v = (J_q + J_r)/(c_q + c_r), \tag{52}$$

where J_q and J_r are the atom fluxes of q and r atoms and c_q and c_r are their concentrations at the plane defined by the wires. Expressions for J_q and J_r can be found from Eq. (49). According to the Gibbs-Duhem relation, $(\partial \ln\gamma_i/\partial \ln N_i)$ will be the same for both species in a binary alloy. Therefore, when these expressions are substituted into Eq. (52), one obtains

$$v = 2\lambda^{-1}B(N_q D_q^* + N_r D_r^*) + (D_q^* - D_r^*)\left(1 + \frac{\partial \ln\gamma_i}{\partial \ln N_i}\right)\frac{\partial N_r}{\partial x}, \tag{53}$$

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

[12] See e.g., A. D. LeClaire, in *Progress in Metal Physics* (Pergamon Press, New York, 1953), Vol. 4, p. 265; D. Lazarus, in *Solid-State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, New York, 1960), Vol. 10, p. 120.

where D_q^* and D_r^* are the values of D^* for q and r atoms; and the mole fractions N_q and N_r of q and r atoms are given by $N_q=c_q/(c_q+c_r)$ and $N_r=c_r/(c_q+c_r)$.

The second term on the right in Eq. (53) is the term found by Darken,[1] while the first term on the right is an additional term which arises from the flow of vacancies. When the expression for B in Eq. (50) is substituted into Eq. (53), it is found that the ratio R of this term to the conventional Darken term is given by

$$R\approx\frac{2}{7.15}\frac{(w_q-w_r)}{(D_q^*-D_r^*)}\frac{(N_qD_q^*+N_rD_r^*)}{(N_qw_q+N_rw_r)}. \tag{54}$$

In a previous paper,[11] it was found that $w_q\approx 4w_r$ when $N_q\approx 0.25$ and $D_q^*\approx 3D_r^*$. It follows from Eq. (54) that $R\approx 0.36$ in this case; and it appears in general that the vacancy flow term in Eq. (53) will not be negligible. Accurate measurements of the Kirkendall shift, $(\partial\ln\gamma_i/\partial\ln N_i)$, D_q^*, and D_r^* in a given alloy would allow values of R and the magnitude of the B term to be determined experimentally. Unfortunately, data in the literature do not allow an unambiguous determination at the present time, since in all cases at least one of the above quantities has not been measured to sufficient accuracy. Such measurements should be quite possible, however. The expression for B in Eq. (50) is only approximate; but it certainly gives the proper sign and general magnitude. Thus, the flow of vacancies should *increase* the Kirkendall shift by a measurable amount.

D. Chemical Interdiffusion Coefficient

Darken[1] has also shown that, if an intrinsic diffusion coefficient D_i for each species i diffusing in a chemical concentration gradient is defined by the equation

$$J_i=-D_i(\partial c_i/\partial x), \tag{55}$$

where J_i is the atom flux of species i with respect to a fixed lattice plane in the crystal, the chemical interdiffusion coefficient $\tilde{D}$ for interdiffusion of the two components q and r in a binary alloy is given by

$$\tilde{D}=N_qD_r+N_rD_q. \tag{56}$$

Values of D_q and D_r can be determined from Eq. (51). When these values are substituted into Eq. (56), one obtains

$$\tilde{D}\approx(N_qD_r^*+N_rD_q^*)[1+(\partial\ln\gamma_i/\partial\ln N_i)] +\frac{2N_qN_r}{7.15}\frac{(D_q^*-D_r^*)(w_q-w_r)}{N_qw_q+N_rw_r}\left(1+\frac{\partial\ln\gamma_i}{\partial\ln N_i}\right). \tag{57}$$

The first term on the right in Eq. (57) is the familiar Darken term, while the second term is an additional contribution arising from the B term in Eq. (51).

This additional term will usually be small but will not always be negligible. For example, if $N_q\approx 0.25$, $D_q^*\approx 3D_r^*$, and $w_q\approx 4w_r$, the ratio of this term to the Darken term equals approximately 0.07.

E. Mean Atom Drift Velocity

The mean atom displacement $\bar{x}$ of a diffusing atom is a quantity of interest in many diffusion experiments. In a cubic crystal, the rate of change of $\bar{x}$ as a function of time t can be expressed in terms of the effective jump frequencies by the equation

$$\frac{\partial\bar{x}}{\partial t}=\lambda\sum_{j=1}^{z}\nu_{oje}\cos\phi_{oj}. \tag{58}$$

Equation (15) will be valid for any site neighboring on the tracer. Thus,

$$\frac{\partial\bar{x}}{\partial t}=\lambda\sum_{j=1}^{z}\nu_{ojb}G_{oj}f_{oj}\cos\phi_{oj}. \tag{59}$$

When values of f_{oj}, ν_{ojb}, and G_{oj} from Eqs. (37), (38), and (39) are substituted into Eq. (59) and use is made of Eqs. (43), (44), and (46), one obtains

$$\frac{\partial\bar{x}}{\partial t}=2D^*\lambda^{-1}\left[A+B+\tfrac{1}{2}\lambda\frac{\partial\ln f}{\partial x}\right], \tag{60}$$

where D^* is given by Eq. (47). If distance is measured in lattice units so that λ is constant, one finds from Eq. (47)

$$\frac{\partial\ln D^*}{\partial x}=\frac{\partial\ln\nu}{\partial x}+\frac{\partial\ln f}{\partial x}, \tag{61}$$

and, with A given by Eq. (48), one finds

$$\frac{\partial\bar{x}}{\partial t}=D^*\left[2\lambda^{-1}B+\frac{\partial\ln D^*}{\partial x}-\frac{\partial\ln\gamma}{\partial x}\right]. \tag{62}$$

The mean atom displacement $\bar{x}$ can be determined experimentally from the profile of a layer of tracer atoms originally located on a plane perpendicular to the direction of a concentration gradient of non-tracer atoms. This can be compared with the value obtained when Eq. (62) is integrated over time and averaged over all tracer atoms.[2,11] In cases where $[(\partial\ln D^*/\partial x)-(\partial\ln\gamma/\partial x)]$ is small, it may be possible to measure the B term in Eq. (62).

5. COMPARISON WITH OTHER DIFFUSION EQUATIONS

A. Le Claire's Continuum Equation

LeClaire,[2] using a continuum approach, has derived an expression for the atom flux J,

$$J=\frac{c\bar{x}}{\tau}-\frac{\langle x^2\rangle_{\text{av}}}{2\tau}\frac{\partial c}{\partial x}-c\frac{\partial}{\partial x}\left(\frac{\langle x^2\rangle_{\text{av}}}{2\tau}\right)+\cdots, \tag{63}$$

where τ is the diffusion time. A similar expression can be obtained from the present atomistic approach. From Eqs. (45), (60), and (61), it follows to first order in small quantities that

$$J = c\partial\bar{x}/\partial t - D^*\partial c/\partial x - c\partial D^*/\partial x. \tag{64}$$

According to Eq. (5), a random walk calculation of $\langle x^2\rangle_{\text{av}}/2\tau$ in a gradient leads to a term in $(\bar{x})^2/\tau$ which may become infinite. This makes the interpretation of Eq. (63) in terms of atom jump frequencies or diffusion coefficients somewhat difficult. However, in the limit where τ goes to zero, $(\bar{x})^2/\tau$ also goes to zero. Thus, if τ goes to zero and the number of jumps n goes to infinity, $\langle x^2\rangle_{\text{av}}/2\tau$ as given by Eq. (5) reduces to D^* as given by Eq. (47), where $\nu = n/\tau$. The higher order terms ($\langle x^3\rangle_{\text{av}}/\tau$; $\langle x^4\rangle_{\text{av}}/\tau$; etc.) in Eq. (63) also go to zero as τ goes to zero. Therefore, Eqs. (63) and (64) agree in this limit. Since Eq. (63) is derived from a continuum approach, it should be most valid in this limit where τ is very small.

It may be noted, however, that the atomistic expression for $\partial\bar{x}/\partial t$ derived by LeClaire[2] is only approximate, since it neglects correlation effects and the effect of a flow of vacancies. Thus, LeClaire's atomistic expression for $\partial\bar{x}/\partial t$ does not agree with Eq. (60) and his resulting expression for J does not agree with Eq. (49).

B. Lidiard's Atomistic Equations

A method proposed by Lidiard,[3] in which the various orientations of vacancy-impurity complexes are considered in detail, can also be used to study diffusion in a gradient. When the same physical assumptions are made, Lidiard's approach should lead to the same expression for J as does the present approach. Recent work[13] confirms this except for some numerical coefficients. The difference in numerical coefficients arises because the non-random return of vacancies which make dissociative w_{jp} jumps is considered in the present paper, while in Lidiard's equations it is not. This difference is not large in the face-centered cubic lattice. However, it becomes more significant in the non-close-packed lattices or in diffusion by an interstitialcy mechanism.

In the present method, the motion of a given atom is followed in detail. This allows $\partial\bar{x}/\partial t$ to be calculated directly without reference to a continuum equation such as Eq. (63). However, in Lidiard's method, this is not possible, so an independent comparison of purely atomistic expressions for $\partial\bar{x}/\partial t$ cannot be made.

C. General Thermodynamic Equations—Cross Terms

Since the flow of vacancies depends on the flow of all the atom species in the crystal, G_{oj} and B depend on the chemical potential gradients of all these species. As a result, Eqs. (49) and (51) for J_i will not reduce to the simple form,

$$J_i = -M(\partial\mu_i/\partial x), \tag{65}$$

where μ_i is the chemical potential of the diffusing species and M is a coefficient of proportionality. Instead, the more general equations,

$$J_i = -\textstyle\sum_k M_{ik}(\partial\mu_k/\partial x), \tag{66}$$

must be used, where μ_k is the chemical potential of species k, the M_{ik} are a set of coefficients, and the sum is over all the different atom species in the crystal.

Equation (66) includes cross terms giving the dependence of the flow of type i atoms on the chemical potential gradients of the other species in the crystal. As LeClaire[2] has pointed out, the correlation factor itself can be absorbed in the constant of proportionality M in Eq. (65). Hence, in the absence of a flow of vacancies, the correlation between the directions of successive atom jumps will not introduce any nonzero cross terms. However, if a flow of vacancies occurs, the cross terms will no longer be zero. Since the vacancy flow depends to a certain extent on the flow of i atoms, the vacancy flow also contributes to the diagonal term in Eq. (66). These additional cross and diagonal terms cause the equation for J_i to differ from that assumed by Darken.

6. INTERSTITIALCY MECHANISM

An analysis very similar to that above can be made when diffusion occurs by an interstitialcy mechanism. In this mechanism, an interstitial atom pushes one of its neighbors from a normal lattice site into an interstitial site and then moves into the lattice site itself. In such a jump, the interstitialcy (which is defined as the lattice imperfection resulting from the presence of an interstitial atom) moves in the same direction as the atoms. Thus, an atom flow toward the right causes an interstitialcy flow also toward the right. This causes interstitialcies to come up to an atom more often from the left than from the right and again leads to G terms which enhance the net atom flow.

In the interstitialcy mechanism, only half of the jumps by a given atom (those from lattice sites to interstitial sites) are correlated to previous jumps, and these depend only on the immediately preceding jump. Thus, the concept of forward jump-correlated reverse jump pairs seems particularly appropriate. The calculation of ν_e follows much the same pattern as in the case of the vacancy mechanism and may be sketched as follows: After an atom has jumped from an interstitial site to a lattice site, there will be an interstitial atom in proper position to cause a reverse jump. Thus, the effective jump frequency ν_{Ioje} for an atom jump from an interstitial site o to a lattice site j is given by

$$\nu_{Ioje} = \nu_{Iojb}(1 - P_{jo}), \tag{67}$$

where P_{jo} is the effective probability of occurrence of

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[13] R. E. Howard and J. R. Manning (to be published).

a correlated reverse jump following an atom jump from site o to site j and ν_{Iojb} is the basic jump frequency for a jump from an interstitial site o to a lattice site j. There is no G factor in Eq. (67), since one does not require an imperfection in a neighboring site to allow an atom to jump from an interstitial site to a lattice site. Also, there are no terms involving P^2, P^3, etc., since correlated jumps occur only in pairs. A fraction P_{oj} of the jumps from a lattice site o to an interstitial site j will merely be correlated reverse jumps which cancel the effect of previous atom jump from interstitial site o to lattice site j. Thus, the effective jump frequency ν_{Loje} for such a jump is given by

$$\nu_{Loje}=G_{oj}\nu_{Lojb}(1-P_{oj}), \tag{68}$$

where the factor G_{oj} arises because interstitialcies may approach a lattice atom more frequently from one direction than another, and ν_{Lojb} is the basic jump frequency for such a jump. The total effective jump frequency ν_{oje} is then given by

$$\nu_{oje}=\nu_{Ioje}+\nu_{Loje}. \tag{69}$$

The number of lattice-to-interstitial jumps taken by a given atom must equal the number of interstitial-to-lattice jumps and $|(1-G_{oj})|\ll 1$. Thus, to first order in small quantities,

$$\nu_{oje}=(1-P_{J/2})(\nu_{Iojb}+G_{oj}\nu_{Lojb}), \tag{70}$$

where $P_{J/2}=\frac{1}{2}(P_{oj}+P_{jo})$. Also, $P_{J/2}=-\langle\cos\theta'\rangle_{\text{av}}$, where θ' is the angle between successive interstitial-to-lattice and lattice-to-interstitial jumps in a homogeneous alloy having the composition associated with the point midway between sites o and j. For an interstitialcy mechanism, the correlation factor f_c in such an alloy is given by[5] $f_c=1+\langle\cos\theta'\rangle_{\text{av}}$. Thus, $1-P_{J/2}=f_c$.

Equation (70) is very similar to Eq. (15), which applies for a vacancy mechanism, the main difference being the form of the correlation factor and the way in which G_{oj} is contained in the equation. The calculation of the atom flux and the mean atom displacement for the interstitialcy mechanism then proceeds in much the same manner as did that for the vacancy mechanism.

7. APPLICATION TO OTHER TYPES OF GRADIENTS

An electric potential gradient or temperature gradient across a crystal can also cause a flow of vacancies or interstitialcies. In fact, any external driving force that tends to make atoms jump more frequently in one direction can cause such a flow. Correlation effects in these cases can be treated in the same manner as in a chemical concentration gradient. In each case, if the correlation factor is a function of position, its value for a given atom jump will be that associated with the point midway between the initial and final atom positions. Also, Eqs. (45) and (60) for the atom flux and mean drift velocity will be valid in these other cases. However, for each type of gradient, the values of A and B must be determined separately from the effect that each gradient has on the various jump frequencies.

If a vacancy or interstitialcy mechanism is operative a flow of vacancies or interstitialcies can be expected when a gradient or external driving force is present. Because of the G terms, this will introduce an additional driving force, tending to make the atoms move in a preferred direction through the crystal. In particular, it will drive the atoms in the same directions as that in which they were already moving under the action of the original driving force. Hence, it will enhance the effect of this force.

8. SUMMARY

Equations describing diffusion in a gradient were derived from an atomistic viewpoint. The displacement of an atom which results from a series of exchanges with a given vacancy was considered. This allowed one to distinguish between (1) correlation effects, which arise because the motion of the tracer atom itself may affect the probability of a vacancy being at the various sites neighboring on the tracer, and (2) vacancy flow effects, which are caused by the non-random motion of atoms other than the tracer. Approximate calculations of the magnitude of the vacancy flow term indicate that the Kirkendall shift in a binary alloy will be significantly *larger* than is predicted by Darken. Also, the effect of the vacancy flow term on the chemical interdiffusion coefficients and the mean tracer displacement may in certain cases be large enough to measure.

Equations (45) and (60) for the diffusion flux and mean drift velocity are quite general and can be applied to diffusion in many kinds of gradients. Their agreement with similar equations can be summarized as follows: Good agreement is found with a generalized form of Lidiard's atomistic equations and with LeClaire's continuum equation in the limit of this equation for very small diffusion times. However, additional terms arising from correlation and vacancy flow effects are found which are not present in LeClaire's atomistic equations or in Darken's continuum equations. These additional terms can appreciably affect various measurable quantities.

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APPENDIX

A. Physical Assumptions to Evaluate *A* and *B*

Equations (45) and (60) will be valid for diffusion in any type of gradient. However, the quantities A and B in these equations depend on the manner in which the gradient changes the various jump frequencies. In the present section, the effect of a chemical concentration gradient on these frequencies will be considered.

To first order in small quantities, the effect will be proportional to the difference between the compositions associated with the initial and final atom positions for a jump. Thus, if differences between the various nontracer atoms are ignored, the jump frequency w_{igh} for exchange of a vacancy on site g with an atom on site h of species i is given by

$$w_{igh}=w_{ighm}(1+\epsilon_i \cos\phi_{gh}), \tag{A1}$$

$$w_{ighm}=w_{ighG}(1+\delta_i \cos\phi_{gh}), \tag{A2}$$

where w_{ighm} is the value of w_{igh} in a homogeneous alloy having the composition associated with the point midway between sites g and h; w_{ighG} is that in a homogeneous alloy having the composition associated with the site g; ϵ_i and δ_i are small quantities; and ϕ_{gh} is the angle between the line g-h and the direction of the gradient. If the gradient lies in the x direction, it follows from Eqs. (14) and (38) that

$$A=\delta_T-\epsilon_T+\lambda(\partial \ln N_v/\partial x), \tag{A3}$$

where the subscript T refers to the tracer ion and N_v is the mole fraction of vacancies. In general,

$$\delta_i=\tfrac{1}{2}\lambda(\partial \ln w_i/\partial x), \tag{A4}$$

and in the case of a chemical concentration gradient, LeClaire finds,[2]

$$\epsilon_i=\tfrac{1}{2}\lambda\left(\frac{\partial \ln\gamma_i}{\partial x}-\frac{\partial \ln\gamma_v}{\partial x}\right), \tag{A5}$$

where γ_i is the activity coefficient for i atoms and γ_v is the activity coefficient for vacancies. If the concentration of vacancies on the average is maintained at its equilibrium value,

$$\partial \ln\gamma_v/\partial x=-\partial \ln N_v/\partial x. \tag{A6}$$

Equation (48) for A then follows in a straightforward manner.[2,11] Further consideration is necessary to derive an equation for B, however, since jumps by several different types of atoms will enter into this calculation, and an average vacancy jump frequency must be defined.

In a binary alloy containing q and r atoms, the average frequency w_{gh} for exchange of a vacancy on site g with an atom on site h is given by

$$w_{gh}=N_{qh}w_{qgh}+N_{rh}w_{rgh}, \tag{A7}$$

where N_{qh} and N_{rh} are the probabilities that a q or r atom will be at site h; and w_{qgh} and w_{rgh} are given by Eq. (A1). For the most part, the composition of the plane containing site h will determine N_{qh} and N_{rh}. However, if the atom arrives at site h neighboring on the vacancy by being originally on site g and then exchanging with this vacancy, the probability that the atom will be a q or r atom will depend on the composition of the plane containing site g. The probability that the atom arrived at site h by this method is approximately z^{-1}, where z is the number of nearest neighbors. Therefore, N_{qh} and N_{rh} in Eq. (A7) are given by

$$N_{ih}\approx(1-z^{-1})N_{iH}+z^{-1}N_{iG}\approx N_{iH}, \tag{A8}$$

where N_{iG} and N_{iH} are the mole fractions of i atoms on the planes containing sites g and h. The approximate equality on the right arises since z^{-1} will be much smaller than unity and N_{iH} differs from N_{iG} only to first order in small quantities. This approximation will not appreciably affect the final expression for B. To first order,

$$N_{iH}=N_{im}[1+\tfrac{1}{2}\lambda \cos\phi_{gh}(\partial \ln N_i/\partial x)], \tag{A9}$$

where N_{im} is the mole fraction of i atoms in a homogeneous alloy having the composition associated with the point midway between sites g and h.

In a binary alloy,

$$\partial N_q/\partial x=-\partial N_r/\partial x, \tag{A10}$$

and the Gibbs-Duhem relation for binary alloys gives

$$\partial \ln\gamma_q/\partial \ln N_q=\partial \ln\gamma_r/\partial \ln N_r. \tag{A11}$$

Thus, Eq. (A7) reduces to

$$w_{gh}\approx w_{ghm}(1+\epsilon \cos\phi_{gh}), \tag{A12}$$

where w_{ghm} is the value of w_{gh} in a homogeneous alloy having the composition associated with the point midway between sites g and h, and

$$\epsilon=-\tfrac{1}{2}\lambda\left[\frac{(w_{qghm}-w_{rghm})}{w_{ghm}}\left(1+\frac{\partial \ln\gamma_i}{\partial \ln N_i}\right)\frac{\partial N_r}{\partial x}+\frac{\partial \ln\gamma_v}{\partial x}\right]. \tag{A13}$$

Similarly,

$$w_{ghm}=w_{ghG}(1+\delta \cos\phi_{gh}), \tag{A14}$$

where w_{ghG} is the value of w_{gh} in a homogeneous alloy having the composition associated with site g, and to first order,

$$\delta=\tfrac{1}{2}\lambda(\partial \ln w/\partial x). \tag{A15}$$

B. Effect of Returning Vacancies

It has been assumed that, even in the presence of a gradient, the effect of vacancies which leave site j and arrive again at some site neighboring on the tracer is the same as if a certain fraction had never left site j at all. This allowed the use of Eq. (9) to calculate the average tracer displacement. In this section, the effect of a gradient on these returning vacancies will be considered in detail, and conditions under which the above assumption is valid will be discussed.

A gradient can change the probability that a vacancy which has made a w_{jp} jump will effectively return to site j. Three cases can be distinguished: (1) the vacancy actually returns to site j, (2) the vacancy jumps directly to some other site k neighboring on the tracer, and (3) the vacancy jumps to a site p not neighboring on the tracer but subsequently arrives at a site k. Cases 1 and 2 can be treated to first order in small quantities. However, the treatment of case 3 is more approximate.

First, let us consider those vacancies which after leaving site j return to this site itself (case 1). To first order, a uniform gradient will change the frequency with which a vacancy makes a given sequence of exchanges with non-tracer atoms by a factor $(1+\epsilon\sum\cos\phi_{gh})$, where ϵ is the same for each jump and the summation is over all jumps in the sequence. For a sequence of jumps which starts and ends at the same site, $\sum\cos\phi_{gh}$ equals zero, so in Eq. (7),

$$w_{jp}Y_{jpa}=w_{jpJ}Y_{jpaJ}, \tag{A16}$$

where w_{jpJ} and Y_{jpaJ} are the values of w_{jp} and Y_{jpa} in a homogeneous alloy having the composition associated with the site j.

Next, let us consider those vacancies which after leaving site j arrive at some other site neighboring on the tracer. A case of particular interest is the face-centered cubic lattice, where it is possible for a vacancy to jump directly from one site neighboring on the tracer to another such site (case 2). In this lattice, the twelve sites neighboring on the tracer can be divided into three groups of four sites each, with all sites in a given group lying on a given (100) plane.[3] For diffusion along an x axis normal to these planes, all sites in a given group are equivalent to one another, and jumps from one equivalent site to another can be treated as if they effectively did not occur. Thus, while jumps between nonequivalent sites contribute to $\nu_{\alpha jo}$ and $w_{\beta jo}$, jumps between equivalent sites do not. Since jumps between equivalent sites are directed normal to the x axis, they are not affected by a gradient along this axis, and in Eq. (7)

$$\sum_{p=1}^{4} w_{jp}Y_{jpe}=\sum_{p=1}^{4} w_{jpJ}Y_{jpeJ}, \tag{A17}$$

where Y_{jpeJ} is the value of Y_{jpe} in the absence of a gradient and the summation is over the four sites which are mutual nearest neighbors of site j and the tracer. In cubic lattices, diffusion will be independent of crystallographic direction, so Eq. (A17) will be valid regardless of the angle between the gradient and the $\langle 100\rangle$ directions.

Next let us consider those vacancies which jump from site j to a site p not neighboring on the tracer and subsequently return to some site k neighboring on the tracer (case 3). When there is a gradient, the net tracer displacement per vacancy averaged over all vacancies can contain a small component normal to the line o-j. When the component is large, Eq. (9) will no longer be a good approximation. If the vacancy concentration at sites not neighboring on the tracer were by some means maintained at their equilibrium values (as is assumed, for example, by Lidiard[3]), the effect of the gradient on the vacancy distribution originating at site j would not result in a net tracer displacement normal to o-j, and the asymmetry in this distribution could be neglected. In real crystals, however, these equilibrium concentrations probably are not maintained, since this would require vacancy sources and sinks at every lattice point. Thus, this matter should be considered further.

If there is a strong attractive force between the tracer and a vacancy at a next-nearest neighbor site p, the fraction of vacancies which move from site j to p and then eventually to a nonequivalent site k may be large. Then the tracer displacement resulting from the asymmetry in the distribution of these vacancies may be large also, and the present treatment will be only roughly correct. On the other hand, if a vacancy at a next-nearest neighbor site is only weakly attracted to the tracer, the error introduced in Eq. (9) will be small. This is probably true in nondilute alloys. Also, this will be true for self-diffusion in a pure lattice or for diffusion of a dilute impurity which is very similar to the solvent atoms. The approximation in Eq. (9) will be particularly good in the diamond lattice where four jumps are required for the vacancy to move from one nearest neighbor site to another.

If there is no strong attractive force between the tracer and a vacancy at a next-nearest neighbor site, Y_{jpaJ} will be considerably larger than the contribution to Y_{jpeJ} from vacancies which have jumped to site p and eventually to a site k. Thus, no great error in the value of $w_{\beta jo}$ will be introduced if the small effect of the gradient on $w_{jp}Y_{jpe}$ is neglected and it is assumed

$$\sum_{p=1}^{z-1} w_{jp}Y_{jpe}=\sum_{p=1}^{z-1} w_{jpJ}Y_{jpeJ}. \tag{A18}$$

In this respect, it may be remembered that the summation in Eq. (A17) is exact.

C. Evaluation of G_{oj} and B

With the aid of Eqs. (A12)–(A18), Eq. (7) can be rewritten as

$$w_{\beta jo}\approx\sum_{p=1}^{z-1} w_{jpJ}[F_{jpJ}+(\delta+\epsilon)\cos\phi_{jp}], \tag{A19}$$

where

$$F_{jpJ}=1-Y_{jpaJ}-Y_{jpeJ}. \tag{A20}$$

Equations (19) and (20) are valid even in a gradient, and equations for $w_{pj}Y_{pja}$ and $w_{pj}Y_{pje}$ can be written analogous to Eqs. (A16) and (A18). When Eqs. (A12) and (A14) are then used to evaluate Eq. (11), one finds

$$\nu_{\alpha jo}=\sum_{p=1}^{z-1}\{N_{vp}w_{pjJ}[1+(\delta-\epsilon)\cos\phi_{jp}] -N_{vj}w_{jpJ}[Y_{jpaJ}+Y_{jpeJ}]\}. \tag{A21}$$

Equilibrium vacancy concentrations probably are not maintained near impurity atoms in the presence of a gradient. However, since $\nu_{\alpha jo}$ is the frequency with which new vacancies come up to site j from other regions in the crystal, local perturbations in the vacancy concentration caused by the motion of the impurity will not affect $\nu_{\alpha jo}$. If the over-all vacancy concentration is maintained at its equilibrium value, the quantities N_{vj} and N_{vp} in Eq. (A21) thus can be replaced by their equilibrium values N_{vjJ} and N_{vpP} in homogeneous alloys having the concentrations associated with sites j and p.

Even when there is a vacancy-impurity binding energy, detailed balance requires

$$N_{vjJ}w_{jpJ}=N_{vpJ}w_{pjJ}, \tag{A22}$$

where N_{vpJ} is the equilibrium concentration of vacancies on a next-nearest neighbor site in a homogeneous alloy having the composition associated with site j. Also,

$$N_{vpP}=N_{vpJ}[1+\lambda\cos\phi_{jp}(\partial\ln N_v/\partial x)], \tag{A23}$$

so Eq. (A21) can be rewritten as

$$\nu_{\alpha jo}=N_{vjJ}\sum_{p=1}^{z-1}w_{jpJ}\times\left[F_{jpJ}+\left(\delta-\epsilon+\lambda\frac{\partial\ln N_v}{\partial x}\right)\cos\phi_{jp}\right]. \tag{A24}$$

When Eqs. (A19) and (A24) are substituted into Eq. (16), one finds

$$G_{oj}=1+\left(\lambda\frac{\partial\ln N_v}{\partial x}-2\epsilon\right)\frac{\sum_{p=1}^{z-1}w_{jpJ}\cos\phi_{jp}}{\sum_{p=1}^{z-1}w_{jpJ}F_{jpJ}}. \tag{A25}$$

It then follows from Eqs. (A6) and (A13) that in a chemical concentration gradient in a binary alloy,

$$G_{oj}\approx1+\lambda\left(\frac{w_q-w_r}{w}\right)\times\left(1+\frac{\partial\ln\gamma_i}{\partial\ln N_i}\right)\frac{\partial N_r}{\partial x}\frac{\sum_{p=1}^{z-1}w_{jpJ}\cos\phi_{jp}}{\sum_{p=1}^{z-1}w_{jpJ}F_{jpJ}}, \tag{A26}$$

where unnecessary subscripts have been omitted. [To first order, the quantities in Eq. (A26) can be taken as those in an alloy having the composition associated with site o.] If all w_{jpJ} are identical and equal the average frequency w, the sum in the numerator in cubic lattices reduces to $w\cos\phi_{oj}$. Also, the sum in the denominator reduces to w_β, with all jump frequencies set equal to w. Values of w_β can be found from Table I. Equation (50) for B then follows upon comparison of Eqs. (39) and (A26).