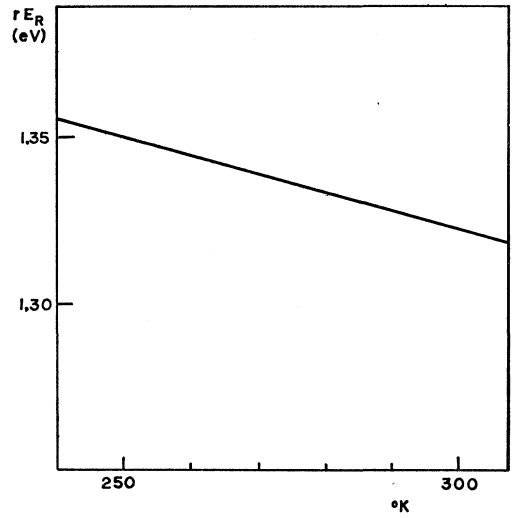

FIG. 4. L_i/L_RE_R of Shockley's expression (1) versus temperature.

Our results are shown in Fig. 3 and one can see that not only do they disagree with those for α particles, but the disagreement is so large that it cannot be easily explained. The parameter L_i/L_RE_R of Shockley's expression is reported in Fig. 4.

According to the assumption that all the charge is generated by a shower following the primary electrons ejected by the incident particle, one cannot expect to find relevant differences from one particle to another, at least in a first approximation. Nevertheless, our results could be explained on the basis of some second-order effect related either to a slight dependence of ϵ_∞ upon the energy of the primary particle (though up to now, there is no evidence for it), or to the fact that different particles have both different spectra of primary electrons and can also lose energy in different ways.

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Correlation Factors for Impurity Diffusion. bcc, Diamond, and fcc Structures

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A general equation for the impurity correlation factor is derived in terms of effective escape frequencies. This equation applies even when the vacancy-jump frequency for association of a vacancy-impurity complex differs from the frequency far from an impurity. Parameters in this equation are calculated for body-centered cubic, diamond, and face-centered cubic structures. In these calculations, it is assumed that vacancy jumps which do not involve a nearest neighbor of the impurity are unaffected by the impurity but that association and dissociation jumps, which do involve nearest neighbors of the impurity, are affected. Analytical expressions for the correlation factor in terms of vacancy-jump-frequency ratios are obtained. In the bcc and fcc structures, results are given for two cases: (A) where all dissociative jumps are equally likely, and (B) where a vacancy which makes a dissociative jump to a second-nearest-neighbor site is still partially bound to the impurity, but vacancies which make dissociative jumps to other sites are not. In the diamond structure, case A cannot be distinguished from case B. Results for the diamond structure and for case A in the fcc structure differ only slightly from previous more approximate results. A comparison is made between the present random-walk method of calculating correlation factors and the pair-association method.

I. INTRODUCTION

WHEN diffusion occurs by a vacancy mechanism, the atoms do not pursue a random walk. Instead, an atom, after exchanging with a vacancy, has a greater-than-random probability of making a reverse jump by re-exchanging with the same vacancy. This causes the atom to pursue a correlated walk and introduces a correlation factor f into the diffusion equations.[1–3]

The correlation factor for impurity diffusion depends on the vacancy-jump frequencies near the impurity.[2,3] Simple expressions for the impurity-correlation factor in terms of vacancy-jump frequencies have been calculated previously for a number of cubic structures.[4] These expressions apply when every vacancy jump from

[1] J. Bardeen and C. Herring, *Atom Movements* (American Society for Metals, Cleveland, 1951), p. 87; also *Imperfections in Nearly Perfect Crystals*, edited by W. Shockley (John Wiley & Sons, Inc., New York, 1952), p. 261.
[2] A. D. LeClaire and A. B. Lidiard, Phil. Mag. 1, 518 (1956).
[3] K. Compaan and Y. Haven, Trans. Faraday Soc. 52, 786 (1956).
[4] J. R. Manning, Phys. Rev. 116, 819 (1959).

a site which is a second-nearest neighbor or farther from the impurity has the same jump frequency. When there is a vacancy-impurity interaction, it is not reasonable to expect the associative jump, which moves a vacancy into a nearest-neighbor position, to have the same frequency as other vacancy jumps originating outside the set of first-nearest neighbors. Consequently, equations were developed which allow the calculation of f in a face-centered cubic structure in terms of this additional frequency.[5] In the present paper, these equations are written in general form and applied to a calculation of f in the body-centered cubic structure. Also, cases where there is special binding at second-nearest-neighbor sites in bcc and fcc structures are considered, and previous calculations for the diamond and face-centered cubic structures are corrected to give somewhat more accurate results for these structures.

II. GENERAL EQUATIONS

In cubic crystals, the correlation factor for diffusion by a vacancy mechanism is given by[2]

$$f=\frac{1+\langle\cos\theta\rangle}{1-\langle\cos\theta\rangle}. \tag{1}$$

Here θ is the angle between 2 successive jumps by a given atom, and the symbol $\langle\ \rangle$ indicates an average over all pairs of successive jumps made by the atom.

The calculation of $\langle\cos\theta\rangle$ is begun by considering an atom M that has just exchanged places with a vacancy V. After this exchange, atom M is on site O and vacancy V is on the neighboring site a. To find $\langle\cos\theta\rangle$, one must calculate the probability that vacancy V will re-exchange with M from the various possible directions.

Complications can arise if, after exchanging with V, atom M exchanges with some other vacancy in the crystal and only later re-exchanges with V. However, at normal vacancy concentrations (less than 10^{-3} mole-fraction) and in the absence of vacancy-vacancy interactions (which might form bound vacancy pairs), this effect is small. When there are no vacancy-vacancy interactions and impurities are present in only dilute concentration, other vacancies in the crystal approach atom M from random directions. Then all contributions to $\langle\cos\theta\rangle$ except those from a re-exchange with V average out to zero; and, for diffusion of a dilute impurity by a single vacancy mechanism, it is a very good approximation to consider only exchanges of M with V. This approximation is made in the following discussion.

If, after the original exchange with M, vacancy V on its next jump re-exchanges with M, just the reverse of the original jump is obtained, and the angle between successive jumps of atom M is 180°. The probability that V and M will re-exchange on this next jump is w_2/R_a, where w_2 is the jump frequency for re-exchange and R_a is the total vacancy jump frequency to sites neighboring on site a. Sites on the first coordination shell (which can be reached in one jump from site O) can be designated as sites β and those in the second coordination shell (which can be reached in two jumps away from site O) as sites γ. Then

$$R_a=w_2+\sum_\beta w_{a\beta}+\sum_\gamma w_{a\gamma}. \tag{2}$$

Here $w_{a\beta}$ and $w_{a\gamma}$ are the vacancy-jump frequencies from site a to sites β and γ, and only sites which can be reached in 1 jump from site a are included in the summations. To a first approximation, we find $\langle\cos\theta\rangle\approx-w_2/R_a$.

Even if V does not immediately re-exchange with M it may eventually return and do so. Therefore, more accurately,

$$\langle\cos\theta\rangle=\frac{w_2}{R_a}(-1)+\sum_\beta\frac{w_{a\beta}}{R_a}\langle\cos\theta_\beta\rangle+\sum_\gamma\frac{w_{a\gamma}}{R_a}\langle\cos\theta_\gamma\rangle. \tag{3}$$

The first term on the right gives the contribution from vacancies which immediately re-exchange with atom M (with $\cos180°=-1$). The terms involving $\langle\cos\theta_\beta\rangle$ and $\langle\cos\theta_\gamma\rangle$ take into account the eventual contributions to $\langle\cos\theta\rangle$ made by vacancies which jump to sites β or γ instead of re-exchanging directly with M. By definition, $\langle\cos\theta_n\rangle$ equals the value of $\langle\cos\theta\rangle$ which would be obtained if, after the atom jump $a-O$, the vacancy V were immediately transported to site n and only then allowed to diffuse and possibly exchange with M. The contribution to $\langle\cos\theta\rangle$ from a vacancy which jumps to site n thus is the probability w_{an}/R_a of jump to site n multiplied by $\langle\cos\theta_n\rangle$. It also follows that $\langle\cos\theta\rangle=\langle\cos\theta_a\rangle$. Consequently, Eq. (3) can be rewritten as

$$\langle\cos\theta\rangle=-w_2\left[R_a-\sum_\beta w_{a\beta}\frac{\langle\cos\theta_\beta\rangle}{\langle\cos\theta_a\rangle}-\sum_\gamma w_{a\gamma}\frac{\langle\cos\theta_\gamma\rangle}{\langle\cos\theta_a\rangle}\right]^{-1}, \tag{4}$$

and, with Eq. (2),

$$\langle\cos\theta\rangle=-w_2\left[w_2+\sum_\beta w_{a\beta}F_\beta+\sum_\gamma w_{a\gamma}F_\gamma\right]^{-1}, \tag{5}$$

where

$$F_\beta=1-\langle\cos\theta_\beta\rangle/\langle\cos\theta_a\rangle, \tag{6}$$

and

$$F_\gamma=1-\langle\cos\theta_\gamma\rangle/\langle\cos\theta_a\rangle. \tag{7}$$

Equation (5) has the form

$$\langle\cos\theta\rangle=-w_2/R_a{}^e, \tag{8}$$

where $R_a{}^e$ is identical with R_a except that $w_{a\beta}$ and $w_{a\gamma}$ are replaced by $w_{a\beta}F_\beta$ and $w_{a\gamma}F_\gamma$.

Equation (8) can be discussed in terms of effective escape or randomization frequencies. If a vacancy V after making a $w_{a\gamma}$ jump returns to site a without having exchanged with atom M, the physical situation is the same as if V had merely remained at site a and had not left this site at all. Any $w_{a\gamma}$ jumps which are followed

[5] J. R. Manning, Phys. Rev. 128, 2169 (1962).

by a return to site a thus do not contribute to the effective frequency of escape from site a and can be treated as if they had never taken place. Vacancies which arrive at other sites β neighboring on M have partially randomized their position with respect to atom M and on average make a smaller contribution to $\langle\cos\theta\rangle$ than if they had returned to site a itself. This has the same effect on $\langle\cos\theta\rangle$ as if a certain fraction of these vacancies returned to site a and the remaining fraction completely escaped. Thus, these vacancies make a partial contribution to the effective frequency of escape. Vacancies which never return to a site neighboring on M contribute fully to the effective escape frequency. In Eq. (5) the fractions F_β and F_γ represent the fractions of $w_{a\beta}$ and $w_{a\gamma}$ jumps which contribute to the effective frequency of escape, and $F_\beta w_{a\gamma}$ and $F_\gamma w_{a\gamma}$ are the effective escape frequencies. The frequency $R_a{}^s$ is the total effective jump-frequency from site a, equal to w_2 plus the effective frequency for escape from site a by exchange with atoms other than M. The fractions $(1-F_\beta)$ and $(1-F_\gamma)$ equal the probabilities that the vacancy will effectively return to site a, either directly or by arriving at some other site β (which is equivalent to a partial return to site a).

Values of $\sum w_{a\beta}F_\beta$ and $\sum w_{a\gamma}F_\gamma$ have been found previously for a number of simple structures where a vacancy jump which originates in the second coordination shell or farther from atom M is assumed to have the same frequency as that in a pure crystal.[4] In the present paper, the calculation is taken one step further. Jumps which do not involve a site in the first coordination shell are still assumed to have a single frequency w_0. However, $w_{\gamma\beta}$ jumps from the second to the first coordination shell are allowed to differ from w_0. Other vacancy-jump frequencies are w_1 from one nearest-neighbor site to another, w_2 for exchange with atom M, and $w_{\beta\gamma}$ from site β in the first coordination shell to site γ in the second coordination shell.

To calculate F_β and F_γ, one must relate $\langle\cos\theta_\beta\rangle$ and $\langle\cos\theta_\gamma\rangle$ to $\langle\cos\theta_a\rangle$. The relation for $\langle\cos\theta_\beta\rangle$ can be found as follows: In the cubic structures considered here, there is at least two- or threefold symmetry around the lines connecting site O to each site β. The vacancy distribution from a vacancy which originates on site β is therefore symmetrical around the line $O-\beta$, and vacancies which start a diffusion path at site β but eventually exchange with atom M along some line other than $O-\beta$ yield on the average no net displacement of M normal to $O-\beta$. As a result, the contribution to $\langle\cos\theta\rangle$ from these vacancies is some factor ζ multiplied by $\cos\theta_\beta$, where θ_β is the angle between the direction $a-O$ and the direction $O-\beta$. Because of the cubic symmetry, the factor ζ must be same for all nearest-neighbor sites β, including site a, and

$$\frac{\langle\cos\theta_\beta\rangle}{\langle\cos\theta_a\rangle}=\frac{\cos\theta_\beta}{\cos\theta_a}=-\cos\theta_\beta. \tag{9}$$

In the face-centered cubic structure, $w_{a\beta}$ jumps are possible to 4 separate β sites, and $\cos\theta_\beta=-\frac{1}{2}$ for each such site. Therefore, $F_\beta=1-\frac{1}{2}=\frac{1}{2}$. In the other structures considered, $w_{a\beta}$ jumps do not occur as nearest-neighbor jumps so, if consideration is restricted to nearest-neighbor vacancy mechanisms, only the F_γ need to be calculated.

To calculate the $\langle\cos\theta_\gamma\rangle$ and F_γ, we may consider a vacancy on a particular site y on the second coordination shell and allow it to diffuse until it arrives either back at site y or at some other site on the first or second coordination shell. If $p_{y\beta}$ and $p_{y\gamma}$ are the probabilities that the first such site at which the vacancy arrives is a given site β on the first coordination shell or a given site γ on the second coordination shell,

$$\langle\cos\theta_y\rangle=\sum_\beta p_{y\beta}\langle\cos\theta_\beta\rangle+\sum_\gamma p_{y\gamma}\langle\cos\theta_\gamma\rangle. \tag{10}$$

Here site y is one of the sites γ, and the summations are over all sites β and γ. One may define quantities U_γ and A_γ

$$U_\gamma=\langle\cos\theta_\gamma\rangle/\langle\cos\theta_a\rangle, \tag{11}$$

$$A_\gamma=-\sum_\beta p_{\gamma\beta}\cos\theta_\beta. \tag{12}$$

It follows from Eqs. (9) and (10) that

$$U_y=A_y+\sum_\gamma p_{y\gamma}U_\gamma. \tag{13}$$

Equations similar to Eq. (13) can be written for each site γ. Since y is a given one of the sites γ, this yields n linear equations relating the n separate U_γ. These can be solved for the U_γ. Then $F_\gamma=1-U_\gamma$.

In the calculation of $p_{y\beta}$ and $p_{y\gamma}$, vacancies which arrive at a site β or γ after leaving y are removed from further consideration. The only vacancies which can arrive at sites β are those that jump directly there on their first jump from y. (Otherwise the vacancy must first arrive at some site on the second coordination shell and be eliminated from further consideration before reaching the first coordination shell.) Consequently, $p_{y\beta}$ merely equals the probability that the vacancy's initial jump from y will take it to site β; and the quantities $p_{y\beta}$ and A_γ are easily determined from the lattice geometry and the jump frequencies $w_{\gamma\beta}$ and w_0. The coefficients $p_{y\gamma}$ are somewhat more difficult to calculate, but even these can be determined to reasonable accuracy in a step-by-step calculation of the probability that the vacancy will arrive at site γ after a given number of jumps.

The number of simultaneous linear equations that must be solved can be reduced by symmetry considerations. All sites γ which are the same distance from site O and whose positive vectors $O-\gamma$ make equal angles with the line $O-a$ are equivalent sites and give the same value of $\langle\cos\theta_\gamma\rangle$. Also sites at the inversion points through site O from these sites γ give the value $-\langle\cos\theta_\gamma\rangle$.

These sites can be grouped together to reduce the number of independent U_γ that need to be treated. For example, if sites q and r have the same $\langle\cos\theta_\gamma\rangle$ and their inversion points are s and t, the contributions from these sites to the summation in Eq. (13) can be combined into one term $(p_{yq}+p_{yr}-p_{ys}-p_{yt})U_q$. The sum $(p_{yq}+p_{yr}-p_{ys}-p_{yt})$ can be called P_{yq}, and sites q, r, s, and t can be said to comprise set q.

III. BODY-CENTERED CUBIC STRUCTURE

In the body-centered cubic structure, site a lies at (1,1,1) from site O. In the second coordination shell (see Fig. 1), the sites at (2,2,2) and $(\bar{2},\bar{2},\bar{2})$ comprise a set which can be called set g. The sites in this set are fifth-nearest neighbors of O. [Fourth-nearest neighbors of O are at sites (3,1,1) on the third coordination shell.] Sites at (2,2,0), (2,0,2), (0,2,2), $(\bar{2},\bar{2},0)$, $(\bar{2},0,\bar{2})$, and $(0,\bar{2},\bar{2})$ form set h and are third-nearest neighbors of O. Sites at $(2,2,\bar{2})$, $(2,\bar{2},2)$, $(\bar{2},2,2)$, $(\bar{2},\bar{2},2)$, $(\bar{2},2,\bar{2})$, and $(2,\bar{2},\bar{2})$ form set i and are fifth-nearest neighbors of O. Sites at (2,0,0), (0,2,0), (0,0,2), $(\bar{2},0,0)$, $(0,\bar{2},0)$, and $(0,0,\bar{2})$ form set j and are second-nearest neighbors of O. The remaining sites X at $(2,\bar{2},0)$, $(\bar{2},2,0)$, $(2,0,\bar{2})$, $(\bar{2},0,2)$, $(0,\bar{2},2)$, and $(0,2,\bar{2})$ are on the symmetry plane normal to $O-a$ and passing through site O. Since there is twofold rotational symmetry around the lines connecting site O to these sites X on the symmetry plane, $\langle\cos\theta_\gamma\rangle$ and U_γ are zero for these sites.

In addition, there is threefold rotational symmetry around the lines $O-g$ and $O-i$. Since groups g and i are both fifth-nearest neighbors of site O, the same argument as that which led to Eq. (9) gives

$$\langle\cos\theta_i\rangle/\langle\cos\theta_g\rangle=\tfrac{1}{3}, \tag{14a}$$

and it follows that

$$U_i=\tfrac{1}{3}U_g. \tag{14b}$$

The considerations above allow one to write Eq. (13) in terms of only three unknowns, U_g, U_h, and U_j

$$U_g=A_g+P_{gg}U_g+P_{gh}U_h+P_{gi}(\tfrac{1}{3}U_g)+P_{gj}U_j, \tag{15}$$

$$U_h=A_h+P_{hg}U_g+P_{hh}U_h+P_{hi}(\tfrac{1}{3}U_g)+P_{hj}U_j, \tag{16}$$

$$U_j=A_j+P_{jg}U_g+P_{jh}U_h+P_{ji}(\tfrac{1}{3}U_g)+P_{jj}U_j. \tag{17}$$

All Dissociative Jump Frequencies Equal

The A_γ and $P_{y\gamma}$ can be calculated in terms of the jump-frequency ratios. In this calculation, one might assume four jump frequencies: w_2 for exchange of a vacancy with atom M, w_3 for a $w_{\beta\gamma}$ jump, w_4 for a $w_{\gamma\beta}$ jump, and w_0 for other jumps (which involve only sites in the second coordination shell or farther from atom M). This allows the associative jump frequency w_4 to differ from w_0. It also assumes that all dissociative jump frequencies $w_{\beta\gamma}$ are equal to one another.

Sites β in the first coordination shell in a body-centered cubic structure can be divided into four sets.

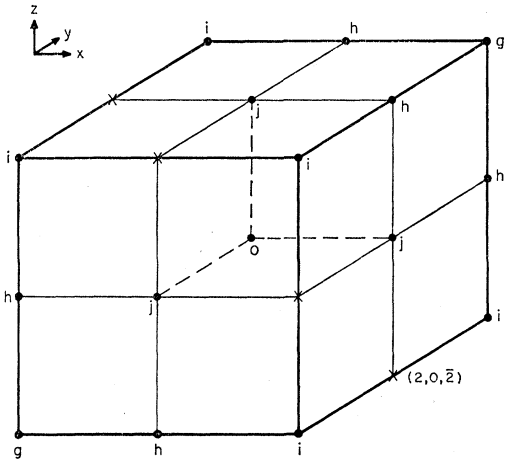

FIG. 1. Body-centered cubic structure. Sites g, h, i, and j are on the second coordination shell from site 0. Site a, not shown, lies at (1,1,1) halfway between sites 0 and g. Sites designated by X are on the symmetry plane passing through site 0 and normal to the line 0–a–g.

Site a at (1,1,1) with $\cos\theta_a=-1$ forms set a, the 3 sites b at $(\bar{1},1,1)$, $(1,\bar{1},1)$ and $(1,1,\bar{1})$ with $\cos\theta_b=-\frac{1}{3}$ form set b, the 3 sites c at $(1,\bar{1},\bar{1})$, $(\bar{1},1,\bar{1})$ and $(\bar{1},\bar{1},1)$ with $\cos\theta_c=\frac{1}{3}$ forms set c, and site d at $(\bar{1},\bar{1},\bar{1})$ with $\cos\theta_d=1$ forms set d. From site g at (2,2,2), site a is the only β site to which the vacancy can jump. Therefore, according to Eq. (12), $A_g=p_{ga}(1)=w_4/R_g$, where R_g is the total jump frequency from site g. (In the present model, $R_g=w_4+7w_0$.) From site h, a vacancy can jump to β sites a and b, so $A_h=w_4(1+\frac{1}{3})/R_h$, where $R_h=2w_4+6w_0$. From site j, jumps to sites a, c, and two separate b sites are possible. Therefore, $j_a=w_4(1+\frac{1}{3}+\frac{1}{3}-\frac{1}{3})/R_j$, where $R_j=4w_4+4w_0$. Probabilities $P_{y\gamma}$ can be determined by a straightforward Bardeen-Herring[1] diffusion-of-probability calculation. One first calculates the probability that the vacancy arrives at various sites on the second coordination shell after one jump from site y. Vacancies which arrive at sites on the first or second coordination shell are removed from further consideration and one proceeds to calculate the probability that the remaining vacancies will arrive at a site on the second coordination shell on the next jump. This can be repeated for as many jumps as necessary.

The $P_{y\gamma}$ for a body-centered cubic structure were calculated by the above method for $y=g$, h, i, or j with $\gamma=g$, h, i, or j. In each case, the vacancy distribution was calculated in detail for 10 jumps, and the probability that a vacancy would arrive at each site on the second coordination shell was determined for these jumps (No. 1–10). Then, the contributions from the remaining jumps (No. 11–∞) were estimated by assuming that successive contributions would continue to decrease in a regular manner. Results are given in Table I. Since approximately 10% of the total contribution to the $P_{y\gamma}$ comes from jumps No. 11–∞, the values in Table I may very well be inaccurate in the second

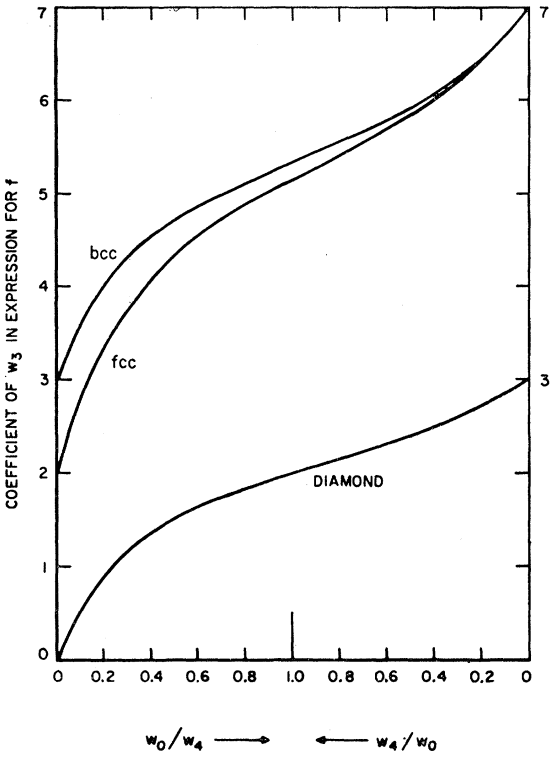

FIG. 2. Values of $7F_3$ for the body-centered cubic and face-centered cubic structures and of $3F_3$ for the diamond structure, calculated from Eqs. (25), (53), and (40), respectively.

decimal place. However, even a first estimate of these values led to a $\langle\cos\theta\rangle$ for self-diffusion (where $w_0=w_2=w_3=w_4$) that agreed to better than three significant figures with the Compaan-Haven values.[3] The final values which appear in Table I were adjusted in a consistent manner to give agreement to almost four significant figures with the Compaan-Haven values. The remaining discrepancy can be attributed to errors introduced from rounding off the $P_{y\gamma}$ to two decimal places.

TABLE I. bcc structure.[a]

$P_{gg}=1.33w_0R_g^{-1}$	$P_{hg}=0.60w_0R_h^{-1}$	$P_{ig}=0.08w_0R_g^{-1}$	$P_{jg}=0.21w_0R_j^{-1}$
$P_{gh}=1.80w_0R_g^{-1}$	$P_{hh}=1.50w_0R_h^{-1}$	$P_{ih}=0.60w_0R_g^{-1}$	$P_{jh}=0.72w_0R_j^{-1}$
$P_{gi}=0.24w_0R_g^{-1}$	$P_{hi}=0.60w_0R_h^{-1}$	$P_{ii}=1.17w_0R_g^{-1}$	$P_{ji}=0.21w_0R_j^{-1}$
$P_{gj}=0.63w_0R_g^{-1}$	$P_{hj}=0.72w_0R_h^{-1}$	$P_{ij}=0.21w_0R_g^{-1}$	$P_{jj}=0.63w_0R_j^{-1}$
$A_g=w_4R_g^{-1}$	$A_h=\frac{4}{3}w_4R_h^{-1}$	$A_i=\frac{1}{3}w_4R_g^{-1}$	$A_j=\frac{4}{3}w_4R_j^{-1}$

[a] Here, $R_g=7w_0+w_4$, $R_h=6w_0+2w_4$, and $R_j=4w_0+4w_4$.

With these values of the $P_{y\gamma}$, solution of Eqs. (15)–(17) gives

$$U_g=\sigma^{-1}[28.85(w_4/w_0)+36.02(w_4/w_0)^2+8(w_4/w_0)^3], \quad (18)$$

$$U_h=\sigma^{-1}[33.82(w_4/w_0)+38.47(w_4/w_0)^2+(16/3)(w_4/w_0)^3], \quad (19)$$

$$U_j=\sigma^{-1}[39.49(w_4/w_0)+22.43(w_4/w_0)^2+(8/3)(w_4/w_0)^3], \quad (20)$$

where

$$\sigma=75.50+146.83(w_4/w_0)+69.46(w_4/w_0)^2+8(w_4/w_0)^3. \quad (21)$$

In our present model, all $w_{\beta\gamma}$ equal w_3. Therefore,

$$\langle\cos\theta\rangle=-w_2\{w_2+w_3[(1-U_g)+3(1-U_h)+3(1-U_j)]\}^{-1}, \quad (22)$$

and, from Eq. (1),

$$f=7w_3F_3/(2w_2+7w_3F_3), \quad (23)$$

where

$$7F_3=1-U_g+3(1-U_h)+3(1-U_j), \quad (24)$$

$$7F_3=\frac{528.50+779.03(w_4/w_0)+267.50(w_4/w_0)^2+24(w_4/w_0)^3}{75.50+146.83(w_4/w_0)+69.46(w_4/w_0)^2+8(w_4/w_0)^3}. \quad (25)$$

It may be noted that $7F_3$ does not go to zero when w_0/w_4 goes to zero, but instead goes to 3. This occurs since the w_4 jump need not return the vacancy directly to site a. A partial escape of the vacancy from this site is possible even when $w_0/w_4=0$. In the other limit, $7F_3$ goes to 7 when w_4/w_0 goes to zero. When $w_4=w_0$, $7F_3=5.33$ (see Fig. 2).

Special Binding at Second-Nearest-Neighbor Sites

It is possible that a vacancy at a second-nearest-neighbor site j to an impurity may be much more strongly bound to the impurity than one at a third-nearest-neighbor site. Then, the true jump frequencies might be approximated by defining frequencies $w_{\beta j}$ from a first- to a second-nearest neighbor, $w_{j\beta}$ from a second- to a first-nearest neighbor, w_{jm} for other jumps from a second-nearest neighbor (to a fourth-nearest-neighbor site), $w_{\beta m}$ from a first- to a third- or fifth-nearest neighbor (sites g, h, or i), w_2 for exchange with the impurity, and w_0 for all other jumps. To avoid any net accumulation of vacancies at sites β, j, or m, it must be true that

$$\frac{c_m}{c_\beta}=\frac{w_{\beta m}}{w_0}=\frac{w_{\beta j}}{w_{j\beta}}\frac{w_{jm}}{w_0}. \quad (26)$$

Here c_m and c_β are the equilibrium vacancy concentration at sites m and β. Also $w_0=w_{m\beta}=w_{mj}$, with m representing a general site that is not a first- or second-nearest neighbor of the impurity but that does neighbor

on such a site. In the present case, sites m include third-, fourth-, and fifth-nearest neighbors of O.

The analysis leading to Eqs. (15)–(17) is valid in general for impurity diffusion in a body-centered cubic structure. In the present model of jump frequencies, the numerical coefficients in the expressions for $P_{y\gamma}$ and A_γ are the same as those in Table I. The only changes needed to make Table I apply in the present case are to set $w_0R_g^{-1}=w_0R_h^{-1}=w_4R_g^{-1}=w_4R_h^{-1}=\frac{1}{8}$, $w_0R_j^{-1}=w_{jm}/(4w_{jm}+4w_{j\beta})$, and $w_4R_j^{-1}=w_{j\beta}/(4w_{jm}+4w_{j\beta})$. Solution of Eqs. (15)–(17) then gives

$$U_g=\sigma^{-1}[42.79(w_{j\beta}/w_{jm})+30.08], \quad (27)$$

$$U_h=\sigma^{-1}[45.34(w_{j\beta}/w_{jm})+32.27], \quad (28)$$

$$U_j=\sigma^{-1}[55.19(w_{j\beta}/w_{jm})+9.39], \quad (29)$$

where

$$\sigma=165.57(w_{j\beta}/w_{jm})+134.21. \quad (30)$$

Equation (5) becomes

$$\langle\cos\theta\rangle=-w_2[w_2+3w_{\beta j}(1-U_j)+w_{\beta m}(4-3U_h-U_g)]^{-1}. \quad (31)$$

With Eq. (26) relating $w_{\beta j}$ to $w_{\beta g}$, Eq. (1) yields

$$f=7Fw_{\beta m}/(2w_2+7Fw_{\beta m}), \quad (32)$$

where

$$7F=\frac{331.14(w_{j\beta}/w_{jm})^2+857.93(w_{j\beta}/w_{jm})+409.95}{165.57(w_{j\beta}/w_{jm})+134.21}. \quad (33)$$

When $w_{j\beta}\gg w_{jm}$, the term $7Fw_{\beta m}$ reduces to $2w_{\beta j}$ and $f=w_{\beta j}/(w_2+w_{\beta j})$. The dependence on $w_{\beta m}$ disappears since, according to Eq. (26), $w_{\beta j}\gg w_{\beta m}$ in this case. Values of $7F$ and $7F(w_{\beta m}/w_{\beta j})$ are shown in Fig. 3.

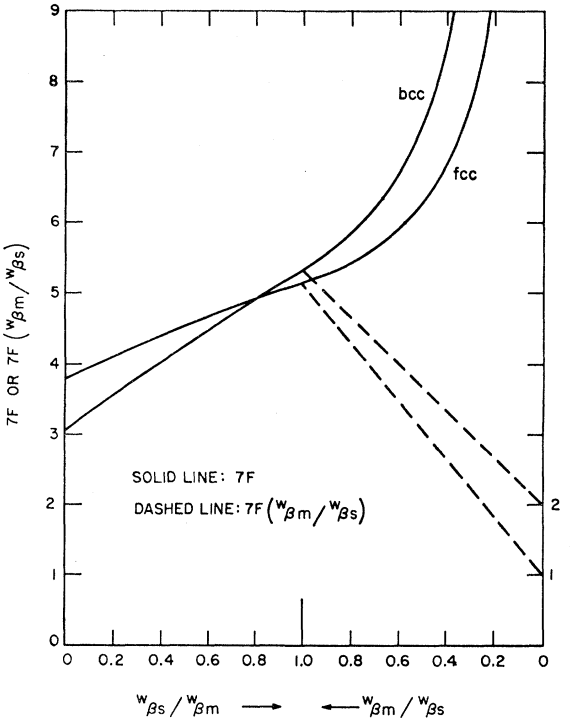

FIG. 3. Values of $7F$ and $7F(w_{\beta m}/w_{\beta s})$ for the body-centered cubic and face-centered cubic structures, calculated from Eqs. (33) and (62). Here $w_{\beta s}$ is the vacancy jump frequency from a first-nearest-neighbor to a second-nearest-neighbor site. For bcc, $w_{\beta s}$ equals $w_{\beta j}$; while for fcc, $w_{\beta s}$ equals $w_{\beta i}$.

IV. DIAMOND STRUCTURE

The preceding method can also be applied to the diamond structure. Here three sets of sites in the second coordination shell can be distinguished (see Fig. 4). If site a is at (1,1,1) from the impurity, sites at (2,2,0), (2,0,2), (0,2,2) form set c. Sites at $(2,\bar{2},0)$, $(\bar{2},2,0)$, $(2,0,\bar{2})$, $(\bar{2},0,2)$, $(0,2,\bar{2})$, and $(0,\bar{2},2)$ form set d, and sites at $(\bar{2},\bar{2},0)$, $(\bar{2},0,\bar{2})$, and $(0,\bar{2},\bar{2})$ form set e. All of these sites are second-nearest neighbors of the impurity. However, there is not full inversion symmetry through the impurity site, so sets c and e cannot be combined. Because of this lack symmetry, $\langle\cos\theta_d\rangle$ will not equal zero, even though set d lies on a plane passing through site O.

One can define vacancy-jump frequencies w_2 for exchange with impurity M, w_3 for jumps from first- to second-nearest neighbors, w_4 for jumps from second- to first-nearest neighbors, w_5 for jumps from second- to third- or fifth-nearest neighbors, and w_0 for jumps originating at third-nearest neighbors or farther from the impurity. The first coordination shell contains the four first-nearest neighbors, the second coordination shell the 12 second-nearest neighbors, and the third coordination shell only the 24 third- and fifth-nearest neighbors. Direct jumps between two first-nearest neighbors are not possible with a nearest neighbor vacancy mechanism nor are jumps between two second-nearest neighbors, so the description above covers all possible jumps. The A_γ

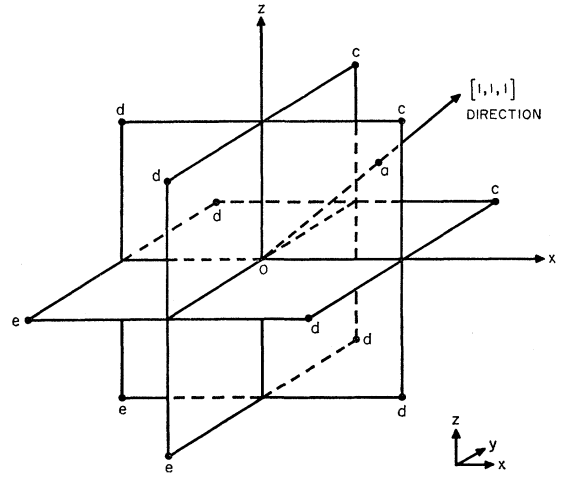

FIG. 4. Diamond structure. Sites c, d, and e are on the second coordination shell from site 0. Site a lies at (1,1,1) in the first coordination shell. The other sites in this shell are at $(1,\bar{1},\bar{1})$, $(\bar{1},1,\bar{1})$, and $(\bar{1},1,\bar{1})$.

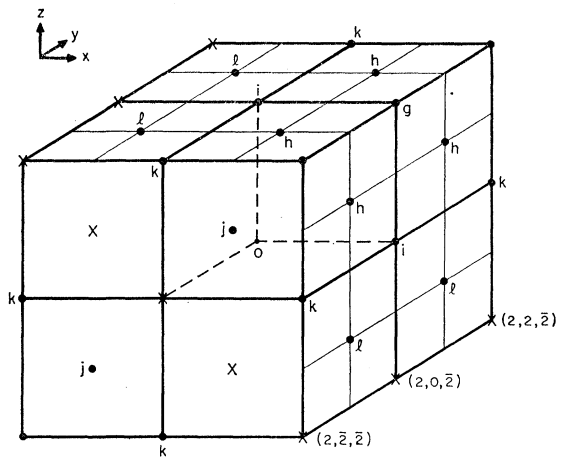

FIG. 5. Face-centered cubic structure. Sites g, h, i, j, k, and l are on the second coordination shell from site 0. Site a, not shown, lies at (1,0,1) half way between sites 0 and g. Sites designated by X are on the symmetry plane passing through site 0 and normal to the line 0–a–g.

and $P_{y\gamma}$ relating U_c, U_d, and U_e for a diamond structure with these jump frequencies are given in Table II. The $P_{y\gamma}$ were calculated by summing contributions from the first 14 vacancy jumps exactly and estimating the contributions from the remaining jumps, while the A_γ were calculated exactly from Eq. (12). Solution of the resulting three simultaneous equations for U_c, U_d, and U_e derived from Eq. (13) gives

$$U_c=\sigma^{-1}[1.40(w_4/w_5)+2.47(w_4/w_5)^2+(w_4/w_5)^3], \quad (34)$$

$$U_d=\sigma^{-1}[-0.31(w_4/w_5)-0.64(w_4/w_5)^2 -\tfrac{1}{3}(w_4/w_5)^3], \quad (35)$$

$$U_e=\sigma^{-1}[-0.79(w_4/w_5)-1.18(w_4/w_5)^2 -\tfrac{1}{3}(w_4/w_5)^3], \quad (36)$$

where

$$\sigma=2.76+6.33(w_4/w_5)+4.52(w_4/w_5)^2+(w_4/w_5)^3. \quad (37)$$

Then, from Eq. (5),

$$\langle\cos\theta\rangle=-w_2[w_2+3w_3(1-U_c)]^{-1}, \quad (38)$$

and, from Eq. (1),

$$f=3w_3F_3/(2w_2+3w_3F_3), \quad (39)$$

where

$$F_3=\frac{2.76+4.93(w_4/w_5)+2.05(w_4/w_5)^2}{2.76+6.33(w_4/w_5)+4.52(w_4/w_5)^2+(w_4/w_5)^3}. \quad (40)$$

For self-diffusion, where $w_2=w_3=w_4=w_5=w_0$, $F_3=\frac{2}{3}$ and f agrees with the Compaan-Haven value[3] of $\frac{1}{2}$. When w_4/w_5 goes to zero, F_3 goes to unity. In the other limit where w_4/w_5 goes to infinity, F_3 goes to zero (see Fig. 2).

Equation (40) is very nearly the same as that found previously[4] by assuming that a certain fraction of vacancies which jumped from a second-nearest neighbor c to a third- or fifth-nearest neighbor would effectively return to site c. In present notation, the expression for F_3 found in this manner was $F_3=[1+\frac{1}{2}(w_4/w_5)]^{-1}$. Since there is a lack of rotational symmetry around the line $O-c$, this assumption of effective returns is not really correct. Nevertheless the expression for F_3 agrees very well with Eq. (40), at the very worst differing by less than 3%. This good agreement is not surprising, since there is a considerable amount of symmetry (though not complete rotational symmetry) around the line $O-c$.

Exact Expressions for F_3 When $w_4=w_5=w_0$

The method of effective return frequencies[4] yields an exact expression for F_3 when $w_4=w_5=w_0$. Since there is threefold rotational symmetry around the line $O-a$, the return of the vacancies which make w_3 jumps from site a to sites on the first coordination shell will have the same effect on $\langle\cos\theta\rangle$ as if a certain fraction $(1-F_3)$ returned to site a itself. Therefore

$$\langle\cos\theta\rangle=-w_2/(w_2+3F_3w_3). \quad (41)$$

For self-diffusion, $w_2=w_3$ and, as shown by Compaan and Haven,[3] $\langle\cos\theta\rangle=-\frac{1}{3}$. By substituting these values into Eq. (41), one finds that F_3 must equal exactly $\frac{2}{3}$ for self-diffusion. If $w_4=w_5=w_0$, a vacancy outside the first coordination shell will diffuse as if it were in a pure crystal, and F_3 will be the same as for self-diffusion. Thus, when $w_4=w_5=w_0$, $F_3=\frac{2}{3}$ and

$$f=w_3/(w_2+w_3). \quad (42)$$

When $w_4=w_5$, this same result is obtained from Eq. (40) or the expression $F_3=[1+\frac{1}{2}(w_4/w_5)]^{-1}$. These expressions therefore are exact when $w_4=w_5$.

V. FACE-CENTERED CUBIC STRUCTURE

In the face-centered cubic structure, there is mirror symmetry across the plane passing through site O normal to the line $O-a$. Therefore $\langle\cos\theta_\gamma\rangle=0$ for any site on this plane. The other 34 sites on the second coordination shell can be divided into 6 sets (see Fig. 5). With site a at (1,0,1) from atom M, sites at (2,0,2) and $(\bar{2},0,\bar{2})$ for example form set g. There are eight sites in set h with a representative site in the first octant being at (2,1,1), four sites in set i are represented by (2,0,0), four in set j are represented by (1,2,1), eight sites in set k are represented by (2,2,0), and eight sites in set l are represented by $(2,1,\bar{1})$. Sets g and k are both fourth-

TABLE II. Diamond structure.[a]

$P_{cc}=4.94w_5R^{-1}$	$P_{dc}=1.70w_5R^{-1}$	$P_{ec}=0.09w_5R^{-1}$
$P_{cd}=3.40w_5R^{-1}$	$P_{dd}=6.03w_5R^{-1}$	$P_{ed}=1.40w_5R^{-1}$
$P_{ce}=0.09w_5R^{-1}$	$P_{de}=0.70w_5R^{-1}$	$P_{ee}=6.94w_5R^{-1}$
$A_c=4w_4R^{-1}$	$A_d=-\frac{4}{3}w_4R^{-1}$	$A_e=-\frac{4}{3}w_4R^{-1}$

[a] Here $R=4(3w_5+w_4)$.

TABLE III. fcc structure.[a]

$P_{gg}=1.04w_0R_g^{-1}$	$P_{hg}=1.39w_0R_h^{-1}$	$P_{ig}=0.20w_0R_i^{-1}$	$P_{jg}=0.08w_0R_h^{-1}$	$P_{kg}=0.10w_0R_g^{-1}$	$P_{lg}=0.05w_0R_h^{-1}$
$P_{gh}=5.56w_0R_g^{-1}$	$P_{hh}=2.20w_0R_h^{-1}$	$P_{ih}=2.68w_0R_i^{-1}$	$P_{jh}=2.44w_0R_h^{-1}$	$P_{kh}=1.52w_0R_g^{-1}$	$P_{lh}=0.28w_0R_h^{-1}$
$P_{gi}=0.40w_0R_g^{-1}$	$P_{hi}=1.34w_0R_h^{-1}$	$P_{ii}=0.50w_0R_i^{-1}$	$P_{ji}=0.06w_0R_h^{-1}$	$P_{ki}=0.20w_0R_g^{-1}$	$P_{li}=1.28w_0R_h^{-1}$
$P_{gj}=0.16w_0R_g^{-1}$	$P_{hj}=1.22w_0R_h^{-1}$	$P_{ij}=0.06w_0R_i^{-1}$	$P_{jj}=0.66w_0R_h^{-1}$	$P_{kj}=1.34w_0R_g^{-1}$	$P_{lj}=0.04w_0R_h^{-1}$
$P_{gk}=0.40w_0R_g^{-1}$	$P_{hk}=1.52w_0R_h^{-1}$	$P_{ik}=0.40w_0R_i^{-1}$	$P_{jk}=2.68w_0R_h^{-1}$	$P_{kk}=1.04w_0R_g^{-1}$	$P_{lk}=1.36w_0R_h^{-1}$
$P_{gl}=0.20w_0R_g^{-1}$	$P_{hl}=0.28w_0R_h^{-1}$	$P_{il}=2.56w_0R_i^{-1}$	$P_{jl}=0.08w_0R_h^{-1}$	$P_{kl}=1.36w_0R_g^{-1}$	$P_{ll}=-0.32w_0R_h^{-1}$
$A_g=w_4R_g^{-1}$	$A_h=\frac{3}{2}w_4R_h^{-1}$	$A_i=2w_4R_i^{-1}$	$A_j=w_4R_h^{-1}$	$A_k=\frac{1}{2}w_4R_g^{-1}$	$A_l=\frac{1}{2}w_4R_h^{-1}$

[a] Here $R_g=11w_0+w_4$, $R_h=10w_0+2w_4$, and $R_i=8w_0+4w_4$.

nearest neighbors of atom M and there is twofold rotational symmetry around the lines $O-g$ and $O-k$. Therefore, as in Eq. (9),

$$\langle\cos\theta_k\rangle/\langle\cos\theta_g\rangle=\cos\theta_k/\cos\theta_g=\tfrac{1}{2}, \tag{43a}$$

and

$$U_k=\tfrac{1}{2}U_g. \tag{43b}$$

In a previous paper,[5] it was assumed that a relation $\frac{1}{3}U_h=\frac{1}{2}U_j=U_l$, similar to Eq. (43b), was valid for the third-nearest neighbors h, j, and l. Since there is not rotational symmetry around the lines $O-h$, $O-j$, and $O-l$, this relation is only approximate. As noted by LeClaire,[6] however, there is still the exact relation,

$$U_h=U_j+U_l. \tag{44}$$

This can be derived from our preceding relation between U_k and U_g. A vacancy which starts from site g can in one jump reach four h sites. A vacancy which makes equivalent jumps from site k would arrive at one h site, one j site, one l site, and one site in the plane where $\langle\cos\theta_\gamma\rangle=0$. Thus, for the relation $\frac{1}{2}U_g=U_k$ to be obeyed, one must have $\frac{1}{2}(4U_h)=(U_h+U_j+U_l+0)$, which reduces to Eq. (44).

Set i contains second-nearest neighbors of M; and U_i is independent of the U_γ for third- and fourth-nearest neighbors.

All Dissociative Jump Frequencies Equal

One can define vacancy-jump frequencies w_2 for exchange with atom M, w_1 for jumps from one first-nearest neighbor to another, w_3 for jumps from a first- to a second-, third-, or fourth-nearest neighbor (first coordination shell to second coordination shell), w_4 for the reverse of a w_3 jump, and w_0 for all other jumps. The A_γ and $P_{y\gamma}$ relating U_g, U_h, U_i, U_j, U_k, and U_l with these jump frequencies are given in Table III. The $P_{y\gamma}$ were calculated by summing contributions from the first six vacancy jumps exactly and estimating the contributions from the remaining jumps, while the A_γ were calculated exactly from Eq. (12). The six equations from Eq. (13) can be reduced to four by Eqs. (43) and (44). Solutions of these equations gives

$$U_g=\alpha\sigma^{-1}(2\alpha^3+29.7\alpha^2+131\alpha+163), \tag{45}$$

$$U_h=\alpha\sigma^{-1}(\tfrac{3}{2}\alpha^3+27.8\alpha^2+140\alpha+187), \tag{46}$$

$$U_i=\alpha\sigma^{-1}(\alpha^3+19.8\alpha^2+118\alpha+215), \tag{47}$$

$$U_j=\alpha\sigma^{-1}(\alpha^3+18.7\alpha^2+95\alpha+122), \tag{48}$$

where

$$\sigma=2\alpha^4+40.2\alpha^3+254\alpha^2+597\alpha+436, \tag{49}$$

and

$$\alpha=w_4/w_0. \tag{50}$$

Since $\sum w_{\alpha\beta}F_\beta=2w_1$, as discussed below Eq. (9),

$$\langle\cos\theta\rangle=-w_2\{w_2+2w_1+w_3[(1-U_g)+4(1-U_h)+2(1-U_i)]\}^{-1}, \tag{51}$$

and

$$f=\frac{2w_1+7F_3w_3}{2w_2+2w_1+7F_3w_3}, \tag{52}$$

where

$$7F_3=7-\left[\frac{10\alpha^4+180.5\alpha^3+927\alpha^2+1341\alpha}{2\alpha^4+40.2\alpha^3+254\alpha^2+597\alpha+436}\right]. \tag{53}$$

When $w_4\ll w_0$, $7F_3=7$; when $w_4=w_0$, $7F_3=5.15$ (in agreement with the Compaan-Haven value for self-diffusion[3]), and when $w_4\gg w_0$, $7F_3=2$ (see Fig. 2).

Values of $7F_3$ from Eq. (53) agree to three significant figures with those obtained previously.[5] In the present work, additional use was made of symmetry properties to estimate the $P_{y\gamma}$. The resulting revision of the $P_{y\gamma}$ accounts for most of the difference in F_3. It was assumed previously that $\frac{1}{3}U_h=\frac{1}{2}U_j=U_l$. When the present values of the $P_{y\gamma}$ are used, the assumption $\frac{1}{3}U_h=\frac{1}{2}U_j=U_l$ changes the F values only in the fifth significant figure. It can be seen from Eqs. (44), (46), and (48) that this relation between U_h, U_j, and U_l is very nearly, but not exactly, obeyed. This is not surprising since $\frac{1}{3}\cos\theta_h=\frac{1}{2}\cos\theta_j=\cos\theta_l$ and there is considerable symmetry, though not complete rotational symmetry, around the lines $O-h$, $O-j$, and $O-l$.

Special Binding at Second-Nearest-Neighbor Sites

There is some evidence, particularly for a divalent impurity in a monovalent sublattice,[7,8] that a vacancy

[6] A. D. LeClaire (private communication).

[7] G. D. Watkins, Phys. Rev. **113**, 79 (1959); **113**, 91 (1959).

[8] R. W. Dreyfus and R. B. Laibowitz, Phys. Rev. **135**, A1413 (1964).

at a second-nearest-neighbor site is strongly bound to the impurity. Then, as in the bcc structure, one might define vacancy jump frequencies $w_{\beta i}$ for jumps from first- to second-nearest neighbors, $w_{i\beta}$ for jumps from second- to first-nearest neighbors, w_{im} for other jumps from second-nearest neighbors, $w_{\beta m}$ for jumps from first- to third- or fourth-nearest neighbors, and w_0 for all jumps from third- or higher order nearest neighbors. To avoid any net accumulation of vacancies at sites β or m, it must be true that

$$\frac{c_m}{c_\beta}=\frac{w_{\beta m}}{w_0}=\frac{w_{\beta i}}{w_{i\beta}}\frac{w_{im}}{w_0}, \tag{54}$$

as in Eq. (26).

In the present model, the numerical coefficients in the expressions for $P_{y\gamma}$ and A_γ are the same as those in Table III. The only changes needed to make Table III apply in the present case are to set $w_0R_i^{-1}=w_{im}/(4w_{i\beta}+8w_{im})$, $w_4R_i^{-1}=w_{i\beta}/(4w_{i\beta}+8w_{im})$, and all other wR^{-1} combinations equal to $\frac{1}{12}$.

Solution for U_g, U_h, U_i, and U_j then gives

$$U_g=\sigma^{-1}[7.28+5.31(w_{i\beta}/w_{im})], \tag{55}$$

$$U_h=\sigma^{-1}[7.80+5.95(w_{i\beta}/w_{im})], \tag{56}$$

$$U_i=\sigma^{-1}[4.02+9.61(w_{i\beta}/w_{im})], \tag{57}$$

$$U_j=\sigma^{-1}[5.45+3.70(w_{i\beta}/w_{im})], \tag{58}$$

where

$$\sigma=32.04+19.22(w_{i\beta}/w_{im}). \tag{59}$$

Equation (5) becomes

$$\langle\cos\theta\rangle=-w_2\{w_2+2w_1+2w_{\beta i}(1-U_i)+w_{\beta m}[4(1-U_h)+(1-U_g)]\}^{-1}. \tag{60}$$

With Eq. (54) relating $w_{\beta i}$ and $w_{\beta m}$, Eq. (1) then yields

$$f=\frac{2w_1+7Fw_{\beta m}}{2w_2+2w_1+7Fw_{\beta m}}, \tag{61}$$

where

$$7F=\frac{121.72+123.03(w_{i\beta}/w_{im})+19.22(w_{i\beta}/w_{im})^2}{32.04+19.22(w_{i\beta}/w_{im})}. \tag{62}$$

When $w_{i\beta}\gg w_{im}$, $7F$ equals $w_{i\beta}/w_{im}$ and

$$f=\frac{2w_1+w_{\beta i}}{2w_2+2w_1+w_{\beta i}}. \tag{63}$$

Values of $7F$ and $7F(w_{\beta m}/w_{\beta i})$ are shown in Fig. 3.

VI. COMPARISON WITH OTHER CALCULATIONS

In Sec. II, general equations for impurity correlation factors are derived. Results for particular crystal structures and jump frequencies are given in Secs. III–V. These results are more general than previous calculations since $w_{\gamma\beta}/w_0$ is allowed to range from zero to infinity and the $w_{\gamma\beta}$ are allowed to differ from one another. Previous calculations usually have included restrictions on $w_{\gamma\beta}/w_0$, for example requiring that $w_{\gamma\beta}=0$[2] or $w_{\gamma\beta}=w_0$[4].

In some crystals, vacancies may be strongly bound to an impurity even when they are third-nearest neighbors or farther from the impurity. Such a situation would require even more detailed calculations than those above. However, the general approach presented in Sec. II could still be applied.

In Refs. 1–5 and in the calculations above, particular vacancies which originally are on site a are followed as they move through the crystal by a more or less random walk, and a resulting $\langle\cos\theta\rangle$ is calculated. This may be called a "random-walk" approach to the calculation of correlation factors. A second general method is the "pair association" method, where the creation, destruction, and reorientation of vacancy-impurity complexes on a number of neighboring planes are followed in detail. It is interesting to compare approximations in the two methods. Lidiard[9] using the pair association method, found $f=(2w_1+7w_3)/(2w_2+2w_1+7w_3)$ for the correlation factor in the face-centered cubic structure. Thus, the coefficient $7F_3$ in Eq. (52) is replaced by 7, which with Eq. (53) would seem to imply $w_4/w_0=0$. Lidiard however did not assume $w_4=0$; on the contrary, he required $w_4\neq0$ with w_4 being related to w_3 by an equation similar to Eq. (26).

The explanation for this apparent paradox is as follows: Vacancy concentrations in Lidiard's model were assumed always to be at their equilibrium values at sites γ on the second coordination shell. Under these conditions, a w_3 jump by a particular vacancy V to a particular site γ cannot cause an increase in the average vacancy concentration at site γ. The effect on $\langle\cos\theta\rangle$ is the same as if vacancy V disappeared upon reaching site γ. In a random-walk model, this is equivalent to saying that return of the particular vacancy V to the impurity is forbidden. Since return of the vacancy is forbidden only when $w_4=0$, one obtains the apparent paradox above. In general, the assumption in the pair association model that the vacancy concentration on site n is maintained at equilibrium leads to the same effect as an assumption in the random-walk model that arrival at site n removes the vacancy from the crystal and prevents it from returning to the impurity.

No arbitrary boundary where vacancies are removed from the crystal is introduced in the present calculations. The calculation of the $P_{y\gamma}$ is still not exact however, since contributions from later vacancy jumps are only estimated. From the agreement which is obtained with the Compaan-Haven values for self-diffusion, one might expect the present results for F to be correct to 3 significant figures. This of course leads to an even smaller error in expressions for the correlation factor f.

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