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Kinetics of Solute-Enhanced Diffusion in Dilute Face-Centered-Cubic Alloys

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A theory of the effect of solutes on solvent self-diffusion in dilute fcc alloys is given, based on the model of nearest-neighbor interactions between solute impurities and vacancies. The parameters of the theory are the four vacancy-jump frequencies in the neighborhood of an impurity and the vacancy-jump frequency in the pure crystal. No assumptions are made about the relative magnitudes of these frequencies. This distinguishes the present theory from previous theories based on the same model. The theory is used to deduce for each of nine dilute Ag-based alloys sets of jump-frequency ratios (and corresponding impurity correlation factors) that are consistent with measured values of the solute enhancement coefficient and of the impurity diffusion coefficient. The desirability of isotope-effect measurements to determine the impurity correlation factors is emphasized.

1. INTRODUCTION

THE effect of impurity additions on solvent self-diffusion has been measured in recent years for several Ag-based alloys (see Table III and the references given there). For small impurity concentrations ($<\sim 2\%$), the change in the self-diffusion coefficient is linear in concentration:

$$D_T(c)=D_T(0)(1+bc), \tag{1}$$

where c is the molar concentration of the solute impurity, $D_T(c)$ and $D_T(0)$ are the diffusion coefficients of a solvent tracer in the alloy and in the pure solvent, respectively, and b is the factor that measures the enhancement (or diminution) of the tracer diffusion coefficient. In some cases, the enhancement can be very large. Thus, adding about 1% of Pb to Ag doubles the Ag diffusion coefficient.

In this paper, we calculate the enhancement factor b on the basis of the nearest-neighbor model of impurity-vacancy interactions.[1] That is, we attribute the enhancement effect to changes in vacancy jump frequencies in the immediate neighborhood of impurities. There have been calculations, on the nearest-neighbor interaction model, of impurity diffusion coefficients.[2,3] There have also been calculations of the enhancement factor b on this model,[4] most recently by Lidiard.[5] However, in earlier calculations of b, assumptions are made, in addition to those inherent in the model, in order to simplify the computations. We avoid such special assumptions in the present calculations.

We describe the calculation of b in Secs. 2 and 3. We find that b is a function of the same three jump frequency ratios as are $D_i/D_T(0)$, the ratio of the impurity diffusion coefficient to that of a solvent tracer, and f_i, the impurity correlation factor. Certain "partial correlation factors" that enter b are calculated numerically as a function of these ratios. Using these calculations, we derive in Sec. 4, for each of nine Ag-based alloy systems, sets of jump frequency ratios and associated values of f_i that are consistent with the measured values of b and $D_i/D_T(0)$ for these systems. We compare our sets of values with those obtained by LeClaire from Thomas-Fermi calculations, and with those obtained by Lidiard from an analysis of experiment using a "weak-binding" approximation for b. Finally, we discuss what information could be obtained from experimental determinations of f_i via isotope effect measurements.

2. FORM OF b ON THE NEAREST-NEIGHBOR INTERACTION MODEL

In the nearest-neighbor interaction model as applied to diffusion in fcc lattices, we distinguish five vacancy jump frequencies, w_0–w_4, which are defined as follows (see Fig. 1): w_1 is the jump frequency of a vacancy

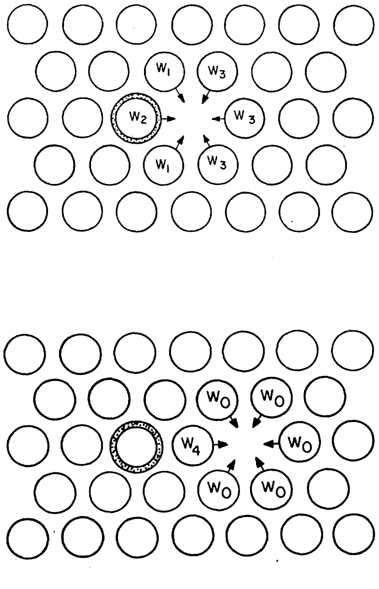

FIG. 1. Vacancy jumps near an impurity in an fcc crystal.

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[1] See, e.g., R. E. Howard and A. B. Lidiard, Rept. Progr. Phys. **27**, 161 (1964).

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

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

[4] R. E. Hoffman, D. Turnbull, and E. W. Hart, Acta Met. **3**, 417 (1955); E. W. Hart, R. E. Hoffman, and D. Turnbull, *ibid.* **5**, 74 (1957); H. Reiss, Phys. Rev. **113**, 1445 (1959).

[5] A. B. Lidiard, Phil. Mag. **5**, 1171 (1960).

between one nearest-neighbor site of an impurity and another nearest-neighbor site, and w_2 that for an impurity-vacancy exchange; w_3 and w_4 are, respectively, the frequencies for jumps from nearest-neighbor to non-nearest neighbor positions and for the reverse jumps. The frequency w_0 describes all other vacancy jumps, i.e., those between sites neither of which neighbors on an impurity, and is assumed to be the same as for vacancy jumps in the pure metal. We calculate the enhancement factor b as a function of these five vacancy jump frequencies by calculating D_T, the tracer diffusion coefficient, to first order in the impurity concentration c.

We begin with the formula [see, e.g., Refs. 6, 7].

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

where x_i is the projection of the ith jump of a tracer along the x axis (taken in a $\langle 100\rangle$ direction); $t(n)$ is the time (on the average) for a tracer to make n jumps. We may write Eq. (2) in the form

$$D_T=\lim_{n\to\infty} f_T\langle\sum_{i=1}^{n} x_i^2\rangle/2t(n)\,, \tag{3}$$

where

$$f_T=1+2\sum_{i=1}^{\infty} \langle x_ix_{i+1}+x_ix_{i+2}+\cdots\rangle/\sum_{i=1}^{\infty}\langle x_i^2\rangle \tag{4}$$

is defined as the tracer correlation factor. Since two-thirds of all tracer jumps have a nonzero projection (all of these of the same length, a) along the x axis, we may write

$$\lim_{n\to\infty}\langle\sum_{i=1}^{n} x_i^2\rangle/2t(n)=\frac{a^2}{3}\lim_{n\to\infty} n/t(n)\,. \tag{5}$$

The quantity $\lim_{n\to\infty} n/t(n)$, the average number of jumps per second made by a tracer, is given by the expression[5] (correct to first order in the concentrations of free vacancies and of impurity-vacancy pairs)

$$\lim_{n\to\infty} n/t(n)=12\left[x_v'(1-7x_f)w_0+\frac{x_p}{3}w_1+\frac{7}{12}x_pw_3 +7x_vx_fw_4\right]. \tag{6}$$

Here x_v is the (molar) concentration of free (unassociated) vacancies, and x_f and x_p are the concentrations of unassociated and associated impurities, respectively ($c=x_f+x_p$). The quantity x_v' is the probability that an unassociated vacancy is at a particular site neighboring a tracer, *given* the presence of tracer. On the present model of impurity-vacancy interactions it follows that[5]

$$x_v=(1-12c)x_v(0)\,, \tag{7}$$

$$x_v'=(1-11c)x_v(0)\,, \tag{8}$$

and also that

$$x_vx_f=\frac{x_p}{12}\frac{w_3}{w_4}\,. \tag{9}$$

In Eqs. (7) and (8), $x_v(0)$ is the concentration of vacancies in a pure crystal. Using Eqs. (7)–(9), we may write Eq. (6) as

$$\lim_{n\to\infty} n/t(n)=12[x_v(0)(1-18c)w_0+(x_p/3) \times(w_1+\tfrac{7}{2}w_3)]\,, \tag{10}$$

where we have neglected terms of order $x_px_v(0)$, since we expect $x_p \ll c$.

We now calculate an expression for f_T, the tracer correlation factor. To do this we distinguish "types" of tracer jumps in the sense defined[8] in Ref. 6. In the present case there are thirteen types of tracer jumps: one type with frequency w_0,[9] two with frequency w_1, five with frequency w_3, and five with frequency w_4. Table I gives examples of jumps of each type along with the relative probabilities c_α ($\alpha=0\cdots12$) that any particular tracer jump having nonzero x projection is of type α. We write Eq. (4) for the correlation factor f_T as[6,7]

$$f_T=1+2\sum_{\alpha=0}^{12} c_\alpha\sum_{i=1}^{\infty}\langle x_\alpha x_{\alpha,i}\rangle/a^2\,, \tag{11}$$

where the subscript α, i denotes the ith jump following an initial jump of type α. We define partial correlation factors f_α by the equation

$$f_\alpha=1+2\sum_{i=1}^{\infty}\langle x_\alpha x_{\alpha,i}\rangle/a^2\,. \tag{12}$$

Then

$$f_T=\sum_{\alpha=0}^{12} c_\alpha f_\alpha\,. \tag{13}$$

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[6] R. E. Howard, Phys. Rev. **144**, 650 (1966).

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

[8] Two tracer jumps A and B with x projections x_A and x_B are of the same "type" if

$$(1)\quad \sum_{i=1}^{\infty}\langle x_Ax_{A,i}\rangle=\sum_{i=1}^{\infty}\langle x_Bx_{B,i}\rangle,$$

and

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

Here the subscripts A, i and B, i refer to the ith jumps following the jumps A and B, respectively. The quantities $p_{i\pm}^{A\beta}$ and $p_{i\pm}^{B}$ are the probabilities that the ith jumps following A and B, respectively, are of type β with x projections in the same (+) or in the opposite (−) directions as the initial jumps.

[9] In principle, there are many types of w_0 jumps depending on the position of the impurity relative to the vacancy. To simplify the discussion, however, we have designated all w_0 jumps as being of a single type. This is consistent with the assumption to be made later that all w_0 jumps have the same partial-correlation factor f_0.

TABLE I. Examples of each of the 13 types of tracer jumps. In each example, the tracer makes a jump from the origin into the vacant site at a (1,1,0). The position of the impurity relative to the tracer and vacancy determines the type of jump. Frequencies appropriate to each type of jump are listed. The quantity c_α is the *a priori* probability that a tracer jump (with nonzero x projection) is of the type α.

Tracer position	Jump frequency	Vacancy position	Impurity position	Type α	$c_\alpha\gamma$[a]
(0,0,0)	w_0	$a(1,1,0)$	Not nearest neighbor of tracer or vacancy	0	$x_v(0)(1-18c)w_0$
(0,0,0)	w_1	$a(1,1,0)$	$a(1,0,1)$	1	$x_pw_1/6$
(0,0,0)	w_1	$a(1,1,0)$	$a(0,1,1)$	2	$x_pw_1/6$
(0,0,0)	w_3	$a(1,1,0)$	$a(2,0,0)$	3	$x_pw_3/12$
(0,0,0)	w_3	$a(1,1,0)$	$a(2,1,1)$	4	$x_pw_3/6$
(0,0,0)	w_3	$a(1,1,0)$	$a(2,2,0)$	5	$x_pw_3/12$
(0,0,0)	w_3	$a(1,1,0)$	$a(1,2,1)$	6	$x_pw_3/6$
(0,0,0)	w_3	$a(1,1,0)$	$a(0,2,0)$	7	$x_pw_3/12$
(0,0,0)	w_4	$a(1,1,0)$	$a(1,-1,0)$	8	$x_pw_3/12$
(0,0,0)	w_4	$a(1,1,0)$	$a(0,-1,1)$	9	$x_pw_3/6$
(0,0,0)	w_4	$a(1,1,0)$	$a(-1,-1,0)$	10	$x_pw_3/12$
(0,0,0)	w_4	$a(1,1,0)$	$a(-1,0,1)$	11	$x_pw_3/6$
(0,0,0)	w_4	$a(1,1,0)$	$a(-1,1,0)$	12	$x_pw_3/12$

[a] $\sum_{\alpha=0}^{12} c\alpha=1$; $\gamma=x_v(0)(1-18c)w_0+(x_p/3)[w_1+(7/2)w_3]$.

Combining Eqs. (3), (5), (10), and (13), we write for D_T

$$D_T=4a^2(\sum_{\alpha=0}^{12} c_\alpha f_\alpha)[x_v(0)(1-18c)w_0+\tfrac{1}{3}x_p(w_1+\tfrac{7}{2}w_3)]. \tag{14}$$

Substituting the expressions for the c_α given in Table I, we have finally

$$D_T=4a^2x_v(0)(1-18c)f_0w_0+\tfrac{1}{3}(4a^2x_p)(\chi_1w_1+\tfrac{7}{2}\chi_2w_3), \tag{15}$$

where

$$\chi_1=\tfrac{1}{2}(f_1+f_2), \tag{16a}$$

and

$$\chi_2=(1/14)(f_3+2f_4+f_5+2f_6+f_7+f_8+2f_9+f_{10}+2f_{11}+f_{12}). \tag{16b}$$

We assume that f_0 is the same for all w_0 jumps and equal to the tracer correlation factor in the absence of impurities. (It may be shown that this assumption introduces only small errors, of the order of 1%, in b). To two significant figures, $f_0=0.78$. The quantities χ_1 and χ_2 are functions of the partial correlation factors f_1–f_{12}. In the next section, we show that these may be calculated as functions of the jump frequency ratios w_4/w_0, w_2/w_1, and w_3/w_1.

We are now in a position to find an expression for b. From Eq. (9)

$$x_p=12x_vx_fw_4/w_3=[12x_v(0)cw_4/w_3][1+0(c)]. \tag{17}$$

Substituting into Eq. (15), we find

$$D_T=D_T(0)(1+bc),$$

where

$$D_T(0)=4a^2x_v(0)f_0w_0, \tag{18}$$

the tracer diffusion coefficient in the absence of impurities, and where

$$b=-18+(4w_4/f_0w_0)(\chi_1w_1/w_3+7\chi_2/2). \tag{19}$$

If we assume that $\chi_1=\chi_2=f_0$, we obtain the same expression for b as found Lidiard in the "weak-binding" approximation[5]

$$b=-18+4(w_4/w_0)(w_1/w_3+\tfrac{7}{2}), \quad \text{(Lidiard)}. \tag{20}$$

The next section shows, however, that the assumption $\chi_1=\chi_2=f_0$ is usually not valid.

3. CALCULATION OF THE f_α

We calculate the partial correlation factors f_α by the method described in Ref. 6. This involves calculating numerically the quantities

$$t^{\alpha\beta}=p_+{}^{\alpha\beta}-p_-{}^{\alpha\beta}, \tag{21}$$

where $p_\pm{}^{\alpha\beta}$ is the probability that, given a tracer jump of type α, the next jump of the tracer (with nonzero projection along the x axis) is of type β with an x-displacement parallel (+) or antiparallel (−) to that of the initial jump. The matrix $\mathbf{T}$ whose elements are the $t^{\alpha\beta}$, and the column vector $\mathbf{f}$ whose components are the f_α are related by the expression[6]

$$\mathbf{f}=\mathbf{1}+2\mathbf{T}(\mathbf{I}-\mathbf{T})^{-1}\mathbf{1}, \tag{22}$$

where $\mathbf{1}$ is the thirteen-component unit column vector and $\mathbf{I}$ the unit 13×13 matrix.

In calculating the $t^{\alpha\beta}$, we follow the procedure given in Ref. 6. A tracer jump of type α is assumed to take place. The path of the vacancy responsible for the jump is followed until it again gives the tracer an x displacement or until it wanders outside a certain specified region. In the latter case, it is assumed that the vacancy returns to the tracer only randomly and thus makes no contribution to the $t^{\alpha\beta}$. The region that we choose within which correlations are considered explicitly contains all configurations where at least one of the particles (impurity, vacancy, or tracer) is the nearest neighbor of the other two. In addition, the region contains all other configurations that can be obtained from these by one jump of the vacancy. As in Ref. 6, we distinguish sets of configurations such that all members of a given set are equivalent (in contributing to tracer diffusion in the x direction). All configurations which are obtained from each other by n-fold rotations around the x axis or by reflection across a mirror symmetry plane containing the x axis are equivalent in this sense. Also, configurations which are obtained by reflection across a mirror symmetry plane passing through the tracer normal to the x axis are negatively equivalent. The latter configurations can be included in a set if their occupation probabilities are weighted by the factor -1. All configurations that lie in the plane containing the tracer normal to the x axis can be neglected since they lead to random motion of the tracer along the x axis. Combining and omitting configurations in this manner leaves 21 sets where one particle is a nearest neighbor of the others, and 98 additional sets making a total of 119 sets. It is easy to see that $t^{\alpha\beta}$, and hence the f_α, are functions only of the ratios w_3/w_1, w_2/w_1, and w_4/w_0. This is because the $t^{\alpha\beta}$ depend only on the relative probabilities of the several kinds of jumps a vacancy can make at each point of its trajectory. If the vacancy is a nearest neighbor of an impurity, it can make jumps of frequency w_1, w_2, and w_3. Hence, the relative probabilities of any particular jump in such a configuration are functions of the ratios w_3/w_1 and w_2/w_1. If the vacancy and impurity are at next-nearest neighbor distances, then the vacancy can make jumps of frequencies w_4 or w_0. The relative probabilities of jumps here are functions only of the ratio w_4/w_0. If the vacancy and impurity are still more widely separated, only w_0 jumps are available and the relative probability of any particular jump is independent of jump frequency.

We have found the f_α numerically as a function of the ratios w_4/w_0, w_3/w_1, and w_2/w_1 making use of an electronic computer. The values of χ_1 and χ_2 found from the f_α via Eqs. (16a) and (16b) are listed in Table II. We note that χ_1 and χ_2 are, respectively, increasing and decreasing functions of w_3/w_1 and of w_2/w_1, when the ratios are varied separately. Both χ_1 and χ_2 are decreasing functions of w_4/w_0. In general, χ_1 and χ_2 are larger or smaller than $f_\alpha=0.78$ depending on the particular set of frequency ratios. We note the strong dependence of χ_1 on w_2/w_1 for small w_3/w_1. In the tight-binding limit ($w_3/w_1=0$), χ_1 vanishes with vanishing w_2/w_1.

We may compare our results in certain special cases with those of more accurate calculations. Thus our values of χ_1 for $w_3/w_1=0$ agree within two significant figures with the calculations of Compaan and Haven.[10] (They also agree within a few percent with the values computed in Ref. 6 where a somewhat smaller region surrounding the tracer was chosen within which correlation effects were considered.) For the case $w_4/w_0=w_3/w_1=w_2/w_1=1$, $\chi_1=\chi_2=0.79$. This is closely equal to the more accurate value of 0.78. On the basis of these comparisons we estimate that our results are meaningful to two significant figures.

4. ANALYSIS OF DATA ON Ag ALLOYS

Table III lists measured values of $D_i/D_T(0)$ (the ratio of the impurity diffusion coefficient to that of a solvent tracer in the pure metal) and of b for nine Ag-based dilute alloys. The values are for the temperature $T=1000°\mathrm{K}$. The table also lists, for each alloy system, sets of the ratios w_4/w_0, w_3/w_1, and w_2/w_1 that are consistent with the measured values of $D_i/D_T(0)$ and b. A range of values of these ratios are consistent with the measured values of b and of $D_i/D_T(0)$, and we have calculated a few sets of values for each alloy system to illustrate trends. To find such sets of ratios we have used Eq. (19) for b, together with the calculated values of χ_1 and χ_2 given in Table II. For the ratio $D_i/D_T(0)$ (also a function only of w_4/w_0, w_3/w_1, and w_2/w_1), we have used the formula[1]

$$D_i/D_T(0)=f_i w_2 w_4/f_0 w_0 w_3\,, \tag{23}$$

where f_i, the impurity correlation factor, is given by the expression

$$f_i=\frac{1+\frac{7}{2}Fw_3/w_1}{1+w_2/w_1+\frac{7}{2}Fw_3/w_1}. \tag{24}$$

The factor F is a function of w_4/w_0 and is calculated numerically in Ref. 3. The values of f_i in Table III are computed for each set of ratios from Eq. (24).

We note that for each alloy the allowed values of w_4/w_0 and also of f_i are bounded, the bounds becoming very narrow for the slow diffusing impurities. For fast diffusing impurities, a wide range of f_i values are consistent with the experimental values of b and $D_i/D_T(0)$ (e.g., for Ge $0\leq f_i\leq 0.71$ depending on the particular set of frequency ratios).

Under certain physical assumptions[11] (which appear to be valid for diffusion by vacancies in fcc crystals), the correlation factor f_i can be found from experiment by measuring the difference in the diffusion coefficients of two isotopes of the given impurity (isotope effect measurements). The only system for which experimental values of all three quantities b, $D_i/D_T(0)$, and f_i are

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

[11] See, e.g., the discussion on p. 656 of Ref. 6.

TABLE II. Values of χ_1 and χ_2 computed as a function of the three jump-frequency ratios w_4/w_0, w_3/w_1, and w_2/w_1.

w_3/w_1	0		0.01		0.02		0.04		0.1		0.25		0.5		1		5		10		100	
	χ_1	χ_2	χ_1	χ_2	χ_1	χ_2	χ_1	χ_2	χ_1	χ_2	χ_1	χ_2	χ_1	χ_2	χ_1	χ_2	χ_1	χ_2	χ_1	χ_2	χ_1	χ_2
w_4/w_0	0																					
w_2/w_1																						
0.001	0.0045	0.999	0.226	0.994	0.322	0.989	0.416	0.980	0.530	0.960	0.644	0.931	0.736	0.906	0.822	0.882	0.949	0.847	0.973	0.840	0.997	0.833
0.01	0.041	0.995	0.238	0.991	0.327	0.987	0.418	0.979	0.530	0.960	0.645	0.931	0.736	0.906	0.822	0.882	0.949	0.847	0.973	0.840	0.997	0.833
0.02	0.074	0.991	0.249	0.989	0.332	0.985	0.420	0.978	0.530	0.959	0.645	0.931	0.736	0.906	0.822	0.883	0.949	0.847	0.973	0.840	0.997	0.833
0.1	0.218	0.973	0.308	0.976	0.363	0.975	0.432	0.972	0.533	0.957	0.646	0.931	0.737	0.907	0.822	0.883	0.949	0.847	0.973	0.840	0.997	0.833
0.5	0.365	0.947	0.397	0.951	0.423	0.954	0.464	0.955	0.545	0.951	0.651	0.933	0.740	0.911	0.824	0.887	0.949	0.849	0.973	0.841	0.997	0.833
1	0.407	0.937	0.429	0.940	0.449	0.943	0.482	0.946	0.554	0.947	0.655	0.933	0.742	0.914	0.826	0.891	0.950	0.851	0.973	0.842	0.997	0.834
2	0.436	0.927	0.454	0.930	0.471	0.933	0.499	0.937	0.564	0.940	0.661	0.934	0.746	0.919	0.828	0.897	0.950	0.854	0.973	0.844	0.997	0.834
10	0.472	0.913	0.486	0.917	0.500	0.919	0.524	0.924	0.581	0.931	0.672	0.934	0.755	0.928	0.835	0.915	0.952	0.873	0.974	0.857	0.997	0.836
1000	0.484	0.908	0.498	0.911	0.511	0.914	0.534	0.919	0.590	0.927	0.678	0.933	0.760	0.933	0.839	0.930	0.955	0.919	0.976	0.916	0.997	0.895
w_4/w_0	0.1																					
w_2/w_1																						
0.001	0.0045	0.997	0.221	0.986	0.316	0.978	0.411	0.967	0.525	0.946	0.640	0.917	0.731	0.893	0.817	0.869	0.946	0.835	0.970	0.828	0.994	0.821
0.01	0.041	0.992	0.232	0.983	0.322	0.976	0.412	0.966	0.526	0.946	0.640	0.917	0.731	0.893	0.817	0.869	0.946	0.835	0.970	0.828	0.994	0.821
0.02	0.074	0.987	0.244	0.980	0.327	0.975	0.415	0.965	0.526	0.946	0.640	0.917	0.731	0.893	0.817	0.870	0.946	0.835	0.970	0.828	0.994	0.821
0.1	0.218	0.964	0.305	0.965	0.360	0.963	0.428	0.959	0.529	0.944	0.641	0.918	0.732	0.894	0.818	0.870	0.946	0.835	0.970	0.828	0.994	0.821
0.5	0.365	0.936	0.396	0.939	0.421	0.941	0.462	0.942	0.541	0.937	0.646	0.919	0.735	0.898	0.820	0.874	0.946	0.836	0.970	0.829	0.994	0.821
1	0.407	0.924	0.428	0.927	0.447	0.930	0.480	0.932	0.550	0.932	0.651	0.920	0.738	0.901	0.821	0.878	0.946	0.838	0.970	0.830	0.994	0.822
2	0.436	0.914	0.454	0.917	0.469	0.920	0.497	0.923	0.560	0.926	0.656	0.920	0.742	0.905	0.824	0.884	0.947	0.842	0.970	0.832	0.994	0.822
10	0.472	0.901	0.486	0.904	0.499	0.907	0.523	0.911	0.579	0.917	0.668	0.920	0.751	0.914	0.831	0.902	0.949	0.860	0.971	0.845	0.994	0.824
1000	0.484	0.896	0.498	0.899	0.510	0.901	0.533	0.906	0.588	0.913	0.674	0.919	0.756	0.919	0.836	0.916	0.953	0.906	0.975	0.902	0.996	0.882
w_4/w_0	1																					
w_2/w_1																						
0.001	0.0045	0.966	0.183	0.930	0.275	0.910	0.372	0.888	0.493	0.857	0.608	0.826	0.699	0.803	0.785	0.781	0.920	0.750	0.946	0.745	0.972	0.739
0.01	0.041	0.955	0.198	0.925	0.283	0.907	0.376	0.886	0.494	0.857	0.609	0.826	0.699	0.803	0.785	0.782	0.920	0.750	0.946	0.745	0.972	0.739
0.02	0.074	0.945	0.213	0.919	0.290	0.904	0.379	0.885	0.494	0.856	0.609	0.826	0.699	0.803	0.785	0.782	0.920	0.750	0.946	0.745	0.972	0.739
0.1	0.218	0.901	0.287	0.892	0.335	0.885	0.399	0.874	0.499	0.854	0.610	0.826	0.700	0.804	0.786	0.783	0.920	0.751	0.946	0.745	0.972	0.739
0.5	0.365	0.854	0.389	0.854	0.409	0.853	0.444	0.852	0.515	0.845	0.616	0.828	0.703	0.808	0.788	0.787	0.920	0.753	0.946	0.746	0.972	0.739
1	0.407	0.840	0.423	0.841	0.439	0.842	0.465	0.842	0.527	0.840	0.621	0.828	0.707	0.812	0.790	0.791	0.921	0.755	0.946	0.747	0.972	0.739
2	0.436	0.830	0.450	0.831	0.462	0.832	0.485	0.834	0.539	0.835	0.628	0.828	0.711	0.816	0.794	0.797	0.922	0.758	0.947	0.749	0.972	0.739
10	0.472	0.817	0.483	0.819	0.493	0.820	0.512	0.823	0.560	0.827	0.641	0.828	0.721	0.824	0.802	0.813	0.927	0.777	0.950	0.762	0.973	0.741
1000	0.484	0.813	0.495	0.815	0.505	0.816	0.523	0.819	0.569	0.823	0.648	0.827	0.727	0.827	0.808	0.824	0.935	0.815	0.959	0.812	0.982	0.796
w_4/w_0	2																					
w_2/w_1																						
0.001	0.0045	0.933	0.157	0.889	0.243	0.864	0.342	0.835	0.467	0.797	0.584	0.762	0.674	0.739	0.760	0.718	0.899	0.689	0.927	0.684	0.955	0.678
0.01	0.041	0.919	0.174	0.882	0.253	0.859	0.346	0.833	0.468	0.796	0.584	0.762	0.674	0.739	0.761	0.718	0.899	0.689	0.927	0.684	0.955	0.678
0.02	0.074	0.906	0.191	0.874	0.263	0.856	0.350	0.830	0.469	0.796	0.584	0.762	0.674	0.739	0.761	0.719	0.899	0.689	0.927	0.684	0.955	0.678
0.1	0.218	0.850	0.275	0.838	0.317	0.829	0.377	0.816	0.476	0.792	0.586	0.763	0.675	0.740	0.761	0.720	0.899	0.690	0.927	0.684	0.955	0.678
0.5	0.365	0.794	0.385	0.793	0.402	0.792	0.431	0.789	0.497	0.781	0.593	0.764	0.679	0.745	0.764	0.725	0.900	0.692	0.927	0.685	0.955	0.678
1	0.407	0.779	0.420	0.779	0.433	0.779	0.456	0.779	0.511	0.776	0.599	0.764	0.682	0.748	0.766	0.729	0.901	0.694	0.928	0.686	0.955	0.678
2	0.436	0.769	0.447	0.770	0.458	0.770	0.477	0.771	0.525	0.770	0.607	0.764	0.687	0.753	0.770	0.736	0.902	0.968	0.928	0.689	0.956	0.679
10	0.472	0.758	0.481	0.759	0.490	0.760	0.506	0.761	0.548	0.763	0.622	0.764	0.699	0.760	0.779	0.751	0.908	0.717	0.933	0.703	0.956	0.681
1000	0.484	0.754	0.493	0.755	0.501	0.756	0.517	0.758	0.557	0.761	0.630	0.763	0.705	0.762	0.786	0.760	0.919	0.752	0.945	0.749	0.969	0.735

TABLE II (*continued*).

w_3/w_1	0		0.01		0.02		0.04		0.1		0.25		0.5		1		5		10		100	
	χ_1	χ_2	χ_1	χ_2	χ_1	χ_2	χ_1	χ_2	χ_1	χ_2	χ_1	χ_2	χ_1	χ_2	χ_1	χ_2	χ_1	χ_2	χ_1	χ_2	χ_1	χ_2
w_4/w_0	5																					
w_2/w_1																						
0.001	0.0045	0.860	0.114	0.818	0.188	0.790	0.282	0.754	0.415	0.704	0.538	0.661	0.628	0.635	0.715	0.614	0.861	0.586	0.892	0.581	0.924	0.576
0.01	0.041	0.843	0.136	0.807	0.203	0.783	0.290	0.750	0.417	0.703	0.539	0.661	0.628	0.635	0.715	0.614	0.861	0.587	0.892	0.581	0.924	0.576
0.02	0.074	0.827	0.158	0.797	0.217	0.775	0.297	0.746	0.419	0.702	0.539	0.661	0.629	0.636	0.716	0.615	0.861	0.587	0.892	0.582	0.924	0.576
0.1	0.218	0.760	0.257	0.748	0.290	0.739	0.340	0.723	0.432	0.695	0.542	0.661	0.629	0.637	0.716	0.616	0.862	0.587	0.892	0.582	0.924	0.576
0.5	0.365	0.695	0.379	0.693	0.391	0.692	0.413	0.688	0.466	0.679	0.552	0.661	0.633	0.642	0.718	0.622	0.862	0.590	0.893	0.583	0.924	0.577
1	0.407	0.680	0.416	0.679	0.425	0.678	0.442	0.677	0.484	0.672	0.560	0.661	0.638	0.646	0.721	0.628	0.863	0.593	0.893	0.585	0.924	0.577
2	0.436	0.670	0.444	0.670	0.451	0.670	0.465	0.669	0.502	0.667	0.570	0.660	0.643	0.650	0.724	0.634	0.864	0.598	0.894	0.588	0.925	0.577
10	0.472	0.661	0.478	0.661	0.484	0.661	0.496	0.661	0.528	0.661	0.589	0.660	0.657	0.656	0.735	0.648	0.871	0.619	0.898	0.605	0.925	0.580
1000	0.484	0.658	0.491	0.658	0.497	0.658	0.508	0.659	0.539	0.659	0.599	0.659	0.666	0.658	0.743	0.655	0.882	0.648	0.911	0.646	0.939	0.635
w_4/w_0	10																					
w_2/w_1																						
0.001	0.0045	0.796	0.0843	0.761	0.144	0.736	0.229	0.699	0.364	0.643	0.495	0.591	0.589	0.560	0.677	0.537	0.830	0.508	0.864	0.503	0.900	0.498
0.01	0.041	0.778	0.110	0.748	0.163	0.726	0.241	0.693	0.367	0.641	0.496	0.591	0.589	0.560	0.677	0.537	0.830	0.508	0.864	0.503	0.900	0.498
0.02	0.074	0.761	0.134	0.736	0.182	0.716	0.252	0.687	0.371	0.638	0.497	0.590	0.589	0.561	0.677	0.537	0.830	0.508	0.864	0.503	0.900	0.498
0.1	0.218	0.689	0.246	0.679	0.270	0.670	0.311	0.656	0.394	0.626	0.501	0.589	0.590	0.562	0.677	0.539	0.830	0.509	0.864	0.504	0.900	0.498
0.5	0.365	0.621	0.375	0.619	0.384	0.617	0.400	0.614	0.442	0.604	0.517	0.586	0.594	0.567	0.678	0.547	0.830	0.512	0.864	0.505	0.900	0.498
1	0.407	0.606	0.413	0.605	0.420	0.604	0.432	0.602	0.465	0.597	0.529	0.585	0.599	0.571	0.680	0.552	0.830	0.516	0.864	0.508	0.900	0.499
2	0.436	0.597	0.442	0.596	0.447	0.596	0.457	0.595	0.486	0.592	0.542	0.584	0.606	0.574	0.683	0.559	0.830	0.522	0.864	0.512	0.900	0.499
10	0.472	0.589	0.476	0.588	0.481	0.588	0.490	0.588	0.515	0.587	0.564	0.583	0.623	0.579	0.695	0.572	0.834	0.545	0.865	0.532	0.899	0.503
1000	0.484	0.586	0.489	0.586	0.493	0.586	0.502	0.586	0.526	0.585	0.575	0.583	0.633	0.581	0.704	0.578	0.842	0.572	0.874	0.570	0.905	0.561
w_4/w_0	100																					
w_2/w_1																						
0.001	0.0045	0.666	0.0343	0.650	0.0612	0.635	0.108	0.610	0.210	0.557	0.352	0.488	0.468	0.440	0.581	0.402	0.788	0.358	0.838	0.351	0.895	0.344
0.01	0.041	0.647	0.066	0.633	0.090	0.621	0.131	0.599	0.224	0.551	0.356	0.486	0.469	0.439	0.581	0.402	0.787	0.358	0.838	0.351	0.895	0.344
0.02	0.074	0.630	0.096	0.618	0.117	0.607	0.153	0.588	0.237	0.544	0.361	0.484	0.470	0.439	0.581	0.403	0.787	0.358	0.838	0.351	0.895	0.344
0.1	0.218	0.558	0.228	0.552	0.238	0.547	0.257	0.537	0.304	0.513	0.389	0.473	0.477	0.438	0.578	0.405	0.783	0.360	0.835	0.352	0.895	0.344
0.5	0.365	0.490	0.369	0.488	0.373	0.487	0.380	0.483	0.400	0.474	0.442	0.457	0.498	0.437	0.575	0.413	0.769	0.367	0.826	0.356	0.894	0.345
1	0.407	0.476	0.409	0.475	0.412	0.473	0.418	0.471	0.433	0.465	0.467	0.452	0.512	0.437	0.577	0.418	0.757	0.374	0.815	0.361	0.892	0.345
2	0.436	0.468	0.439	0.467	0.441	0.466	0.446	0.465	0.459	0.460	0.488	0.450	0.527	0.439	0.582	0.424	0.742	0.384	0.801	0.369	0.889	0.347
10	0.472	0.462	0.474	0.461	0.476	0.461	0.480	0.460	0.493	0.456	0.519	0.450	0.554	0.443	0.602	0.433	0.722	0.408	0.763	0.395	0.868	0.356
1000	0.484	0.460	0.487	0.460	0.489	0.459	0.493	0.458	0.505	0.456	0.532	0.450	0.567	0.445	0.615	0.438	0.728	0.428	0.757	0.426	0.790	0.419
w_4/w_0	10^5																					
w_2/w_1																						
0.001	0.0045	0.641	0.0257	0.628	0.0455	0.616	0.0811	0.595	0.165	0.547	0.297	0.478	0.419	0.424	0.547	0.380	0.807	0.325	0.877	0.316	0.959	0.307
0.01	0.041	0.622	0.059	0.611	0.076	0.600	0.108	0.582	0.183	0.539	0.305	0.475	0.421	0.424	0.547	0.380	0.806	0.325	0.876	0.316	0.959	0.307
0.02	0.074	0.605	0.090	0.595	0.105	0.586	0.132	0.570	0.200	0.531	0.313	0.472	0.423	0.423	0.546	0.380	0.805	0.325	0.875	0.316	0.959	0.307
0.1	0.218	0.533	0.225	0.528	0.232	0.524	0.246	0.515	0.283	0.493	0.355	0.456	0.439	0.419	0.544	0.383	0.796	0.328	0.869	0.318	0.958	0.307
0.5	0.365	0.466	0.368	0.465	0.371	0.463	0.376	0.460	0.392	0.451	0.426	0.433	0.473	0.413	0.544	0.389	0.764	0.338	0.844	0.325	0.954	0.308
1	0.407	0.452	0.409	0.451	0.411	0.450	0.415	0.448	0.427	0.441	0.454	0.428	0.492	0.413	0.549	0.393	0.741	0.347	0.821	0.331	0.949	0.309
2	0.436	0.445	0.438	0.444	0.440	0.443	0.444	0.441	0.454	0.436	0.478	0.426	0.510	0.414	0.557	0.398	0.716	0.357	0.790	0.341	0.940	0.311
10	0.472	0.439	0.474	0.439	0.475	0.438	0.479	0.437	0.489	0.433	0.511	0.426	0.540	0.418	0.581	0.407	0.688	0.381	0.730	0.368	0.886	0.325
1000	0.484	0.438	0.486	0.437	0.488	0.437	0.491	0.436	0.502	0.432	0.524	0.427	0.553	0.420	0.595	0.412	0.696	0.400	0.723	0.398	0.754	0.390

TABLE III. Jump-frequency ratios w_4/w_0, w_3/w_1, and w_2/w_1 for impurities in Ag at $T=1000°\text{K}$. These are found from Eqs. (19) and (23) with values of b and $D_i/D_T(0)$ for $T=1000°\text{K}$ as interpolated from experimental results. The values of f_i are deduced from Eq. (24) for each set of frequency ratios. LeClaire's calculated ratios (Ref. 14) are given for certain of the impurities, with the corresponding f_i calculated from Eq. (24). Also given are values of f_i in Lidiard's "weak-binding" approximation (Ref. 5) and the value of f_i for Cd deduced by Schoen (Ref. 13) from isotope effect measurements.

	w_4/w_0	w_3/w_1	w_2/w_1	f_i	
	0	0	0.075	0.93	
Sb	1.0	0.03	0.22	0.83	
$b=65.7$[a]	2.0	0.09	0.34	0.78	
$D_i/D_T(0)=7.60$[b]	5.0	0.69	1.32	0.62	
	6.0	1.35	2.30	0.58	
	8.62	∞ ($w_2/w_3=1.34$)	∞	0.51	
	2.2	1.35	71.4	0.05	(LeClaire)
				0.64	(Lidiard)
Pb	0	0	0.10	0.91	
$b=87$[c]	1	0.02	0.23	0.82	
$D_i/D_T(0)=11$[c]	2	0.06	0.33	0.78	
	11.0	∞ ($w_2/w_3=2.0$)	∞	0.40	
				0.65	(Lidiard)
Ge	0	0	0.42	0.71	
$b=27$[c]	1	0.09	1.4	0.48	
$D_i/D_T(0)=9.4$[d]	2	0.39	6.2	0.23	
	3.1	2.4	∞	0.00	
				0.39	(Lidiard)
Tl	0	0	0.24	0.81	
$b=37$[d]	1	0.06	0.63	0.65	
$D_i/D_T(0)=8.4$[d]	2	0.22	1.4	0.52	
	4.87	∞ ($w_2/w_3=6.9$)	∞	0.19	
				0.50	(Lidiard)
In	0	0	0.21	0.82	
$b=18$[e]	1	0.13	0.95	0.59	
$D_i/D_T(0)=5.3$[f]	2	0.81	4.3	0.39	
	2.95	∞ ($w_2/w_3=5.3$)	∞	0.26	
	1.6	1.2	19	0.16	(LeClaire)
				0.43	(Lidiard)
	0	0	0.17	0.85	
Cd	0.5	0.067	0.57	0.68	
$b=9.2$[e]	1.0	0.26	1.4	0.54	
$D_i/D_T(0)=3.7$[f]	1.5	0.9	3.9	0.45	
	2.0	7.0	27	0.38	
	2.13	∞ ($w_2/w_3=3.8$)	∞	0.36	
	1.3	1.1	6.8	0.36	(LeClaire)
				0.52	(Lidiard)
				<0.1	(Schoen, isotope effect)
Au	0	No solution			
$b=-1.2$[g]	0.13	0 ($w_2/w_3=1.6$)	0	1.00	
$D_i/D_T(0)=0.26$[g]	1	1.5	0.31	0.94	
	1.3	∞ ($w_2/w_3=0.17$)	∞	0.94	
Cu	0	No solution			
$b=8.1$[c]	0.2	0 ($w_2/w_3=4.3$)	0	1.00	
$D_i/D_T(0)=1.1$[h]	1.0	0.29	0.29	0.86	
	2.0	12	10	0.82	
	2.14	∞ ($w_2/w_3=0.49$)	∞	0.81	
				0.86	(Lidiard)
Pd	0	No solution			
$b=-8.2$[i]	0.08	0 ($w_2/w_3=0.4$)	0	1.00	
$D_i/D_T(0)=0.040$[j]	0.73	∞ ($w_2/w_3=0.04$)	∞	0.98	

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available is the alloy Ag-Cd.[12] Referring to Table III, we see that the three experimental values for this system are inconsistent: The measured value of f_i[13](<0.1) lies well below the smallest value (0.36) that is consistent with the measured values of b and $D_i/D_T(0)$. It is important that the isotope effect measurement (which is a difficult one) be repeated for Ag-Cd. If the isotope effect result is confirmed, then either the nearest-neighbor model [upon which Eqs. (19), (23), and (24) are based] is inadequate, or else the theoretical interpretation of the isotope effect measurement to yield f_i is incorrect. It is very desirable that isotope effect measurements be made for other impurities. For slow diffusers (such as Pd) the correlation factor is closely predicted from the known values of b and $D_i/D_T(0)$. In such cases, isotope measurements would provide a good test of theory. For the case of fast diffusers, isotope effect measurements (if they reliably yield f_i) could specify which of the allowed correlation factors, and hence which set of jump frequency ratios, is correct.

LeClaire[14] has calculated jump frequency ratios for impurities in Ag on the basis of a Thomas-Fermi model of impurity-vacancy interaction. In cases where the impurity is in the same row in the periodic table as Ag, LeClaire's values are consistent with measured values of $D_i/D_T(0)$. We list the calculated jump frequency ratios for such impurities in Table III, and values of f_i computed from these ratios. We note that for impurities of valence greater than one, LeClaire's values of w_3/w_1 and w_2/w_1 are too large, given his calculated value of w_4/w_0. The discrepancy between LeClaire's values and those consistent with the measured values of b and $D_i/D_T(0)$ become larger, the larger the impurity valence. The fact that LeClaire's calculations may underestimate impurity-vacancy binding (making w_3 too large) and overestimate the frequency of impurity-vacancy exchanges (making w_2 too large) has been pointed out by Corless and March.[15]

We have also listed in Table III the values of f_i as computed by Lidiard, from the experimental data on b and $D_i/D_T(0)$, in the weak-binding approximation [using Eq. (20) for b and Eqs. (23) and (24) in the approximation $F=1$ for $D_i/D_T(0)$]. These fall always within the allowed range of f_i.

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[12] There is a measurement of the isotope effect of Fe in Ag and in Cu [J. G. Mullen, Phys. Rev. **121**, 1649 (1961)]. However, no measurements of b for these systems are available. *Footnote added in proof.* S. J. Rothman and N. L. Peterson [this issue, Phys. Rev. **154**, 552 (1967)] have recently made measurements of f_i and $D_i/D_T(0)$ for zinc impurity diffusing in silver and of b for silver diffusing in dilute silver-zinc alloys. Their experimental values of b and $D_i/D_T(0)$ yield an allowed range of f_i similar to that for Cd in Table III. Their experimental f_i values lie comfortably within this range (in contrast to the case for Cd). From the three measured quantities [b, $D_i/D_T(0)$, and f_i] and the three equations (19), (23), and (24), the three jump-frequency ratios [w_4/w_0, w_3/w_1, and w_2/w_1] for zinc in silver can be calculated. The results (explicit values are quoted in Rothman and Peterson's paper) indicate that w_4/w_0 and w_2/w_1 in the range 747–880°C are somewhat larger than unity, while w_3/w_1 is smaller than unity.

[13] A. H. Schoen, Phys. Rev. Letters **1**, 1662 (1955).

[14] A. D. LeClaire, Phil. Mag. **7**, 141 (1962). LeClaire calculates the differences in activation energies for jumps of the various frequencies and finds the ratios w_3/w_1 and w_4/w_0 from such differences in energies by assuming that the pre-exponential factors for the frequencies w_1-w_4 are the same (all these jumps involve normal ions). LeClaire allows that the pre-exponential factor for the frequency w_2 may be different and finds the ratio of pre-exponentials ν_2/ν_0 from Eqs. (23) and (24) making use of calculated values of activation energy differences and experimental values of $D_i/D_T(0)$. LeClaire makes the assumption, however, that $F=1$ in Eq. (24). In deriving w_2/w_1 from LeClaire's activation energies, we do not make this assumption but use the accurate values for F given in Ref. 3. Therefore the values w_2/w_1 (and also those of f_i) that we attribute to LeClaire are different from those given in LeClaire's paper.

[15] G. K. Corless and N. H. March, Phil. Mag. **7**, 1765 (1962).