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Correlation Coefficient and the Isotope Effect for the Diffusion of Zinc in Silver*

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The correlation factor f_i for the diffusion of zinc in silver has been obtained from measurements of the diffusion of Zn^{65} and Zn^{69} in silver single crystals. f_i increases from 0.47 at 697°C to 0.56 at 952°C. The values of f_i and their temperature dependence agree with those calculated by LeClaire. The self-diffusion coefficients of silver in silver-zinc alloys containing 0 to 4 at.% zinc have been measured at 747 and 880°C. The relative jump frequencies of the zinc atoms and the silver atoms, which are neighbors of the zinc atom, have been calculated from these data, using the theory of Howard and Manning and the results of the isotope-effect experiments. Values of f_i calculated from these data by means of Lidiard's theory are also in agreement with the values obtained from the isotope effect.

INTRODUCTION

THE correlation factor f_i for the diffusion of an impurity is important because of the information it can give on the relative magnitudes of the jump frequencies of the impurity and host atoms.[1,2] Experimental values of f_i for diffusion in metals can be obtained from a measurement of the isotope effect in diffusion[3,4] or from the effect of solute on the self-diffusion of the solvent.[5] By combining the results of these two types of experiments, the ratios of various atomic-jump frequencies can be obtained.[6] This paper presents such results for the diffusion of zinc in silver.

The exact form of the correlation factor depends on the mechanism of diffusion and on which solvent atom jumps are considered to be influenced by the presence of the solute. Since the vacancy mechanism is established for diffusion in silver,[7] the simplest form of the correlation factor is[1]

$$f_i=\frac{w_1+\frac{7}{2}w_3}{w_1+w_2+\frac{7}{2}w_3}. \tag{1}$$

Here w_1 is the rate of exchange of a vacancy neighboring an impurity atom with any of the four solvent atoms that are also neighbors of the impurity; w_3 is the rate of exchange of a vacancy neighboring an impurity with any of the seven solvent atoms adjacent to the vacancy but not neighbors of the impurity (dissociation jump); and w_2 is the impurity-vacancy exchange rate. A more detailed treatment,[2] which includes the effect of returning vacancies, gives

$$f_i=\frac{w_1+\frac{7}{2}Fw_3}{w_1+w_2+\frac{7}{2}Fw_3}, \tag{1a}$$

where F is a function of w_4/w_0, w_4 is the frequency of the association jump (reverse of a w_3 jump), and w_0 is the frequency of solvent-vacancy exchanges in the pure solvent lattice.

The jump frequencies depend on temperature exponentially:

$$w_j=\nu_j\exp(-H_j/RT), \tag{2}$$

where the ν_j's are the vibration frequencies and the H_j's are the activation energies. Since, in general, the H_j's will not be equal, f_i will vary with temperature nonexponentially.

The relation between the correlation factor and the isotope effect is given by[3,4]

$$\left(\frac{D_\alpha}{D_\beta}-1\right)=f_\alpha\left(\frac{w_2{}^\alpha}{w_2{}^\beta}-1\right)=f_\alpha\left(\frac{\nu_2{}^\alpha}{\nu_2{}^\beta}-1\right), \tag{3}$$

where the D's, w_2's, and ν_2's are the diffusion coefficients, jump frequencies, and vibration frequencies, respectively, of the isotopes of mass m_α and m_β, and it has been assumed that H_2 is not a function of mass.[8] Since $f_i=f_\alpha$ within 0.14% for the isotopes used in this work,[8] f_i will be used throughout the rest of this paper. If $\nu_2\propto m^{-1/2}$, as expected from a simple harmonic model,

$$(D_\alpha/D_\beta-1)=f_i((m_\beta/m_\alpha)^{1/2}-1). \tag{4}$$

However, a more rigorous treatment that includes many-body interactions at the saddle point[9] shows that ν_2 may not be proportional to $m^{-1/2}$ and that a correction factor for this should be included. Equation (4) then becomes[10]

$$(D_\alpha/D_\beta-1)=f_i\Delta K((m_\beta/m_\alpha)^{1/2}-1). \tag{5}$$

The correction factor ΔK is the fraction of the translational kinetic energy, associated with motion in the jump direction, that is possessed by the jumping atom at the saddle point. To get f_i from an isotope-effect measurement, one must first measure ΔK. This can be done by measuring the isotope effect for self-diffusion,

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* This work was performed under the auspices of the U. S. Atomic Energy Commission.

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

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

[3] A. H. Schoen, Phys. Rev. Letters **1**, 138 (1958).

[4] K. Tharmalingam and A. B. Lidiard, Phil. Mag. **4**, 899 (1959).

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

[6] R. E. Howard and J. R. Manning (private communication).

[7] R. O. Simmons, J. S. Koehler, and R. W. Balluffi, *Radiation Damage in Solids* (International Atomic Energy Agency, Vienna, 1962), Vol. I, p. 155.

[8] A. D. LeClaire, Phil. Mag. **14**, 1271 (1966).

[9] G. H. Vineyard, J. Phys. Chem. Solids **3**, 121 (1957).

[10] J. G. Mullen, Phys. Rev. **121**, 1649 (1961).

since f for this case can be calculated if the diffusion mechanism is known. Measurements of ΔK for the fcc crystals Pd,[11] NaCl,[12] and Ag [13] have given ΔK close to 1 (1.02 ± 0.04, 0.93 ± 0.09 and 0.86 ± 0.05, respectively); ΔK for bcc Na [14] is surprisingly small (0.52 ± 0.05).

The relation between f_i and the effect of solute on solvent self-diffusion is given by the equations[5]

$$D_S(C)=D_S(0)(1+bc) \tag{6}$$

and

$$f_i=1-\frac{4f_0}{b+18}\left(\frac{D_i}{D_s(0)}\right), \tag{7}$$

for diffusion in fcc alloys. Here $D_S(0)$ is the self-diffusion coefficient in the pure solvent, $D_S(C)$ is the solvent-diffusion coefficient in a dilute binary alloy containing atomic fraction c of solute, D_i is the impurity diffusion coefficient in the pure solvent, f_0 is the correlation factor for self-diffusion in the pure solvent, and b is a constant. In the derivation of Eqs. (6) and (7) (Lidiard's theory), Eq. (1) was used for f_i. One of the objects of this work was to check the validity of Lidiard's theory by comparing the f_i's measured by these two methods.

Values of the jump-frequency ratios can be calculated from our experimental data by means of Howard's and Manning's theory,[6] which uses Eq. (1a) for f_i and removes some other restrictions inherent in Lidiard's theory. This theory gives a range of possible values of f_i for a given set of values of D_i, $D_S(0)$ and b, and unique values of w_4/w_0, of w_3/w_1, and of w_2/w_1 for each value of f_i.

Numerical values of f_i and of the temperature dependence of the w_j's have been calculated from the electronic structures of the solvent and solute by LcClaire.[15] The results of this theory can be compared with our measurements in two ways. The first is a direct comparison of f_i values obtained from the isotope-effect measurements with the ones calculated by LeClaire. The second is a comparison of jump-frequency ratios, calculated from our data by means of Howard's and Manning's theory with those calculated by LeClaire.

The silver-zinc system was chosen for this study because (1) ΔK is known for silver self-diffusion,[13] (2) a pair of zinc isotopes suitable for an isotope effect measurement can be made easily, and (3) Zn is an electropositive impurity in silver and should thus have an appreciably temperature-dependent f_i.[15]

EXPERIMENTAL PROCEDURE

Isotope Effect for the Diffusion of Zinc in Silver

The two zinc isotopes, Zn^{65} and Zn^{69}, were diffused simultaneously from a thin layer on the surface. The solution of the diffusion equation for these boundary and initial conditions is

$$c=\text{const}\exp(-x^2/4Dt), \tag{8}$$

where c is the concentration or specific activity of the tracer at a distance x from the surface of the crystal, and t the time of diffusion. The ratio of the concentrations of the two isotopes as a function of penetration is given by[3,12]

$$\begin{aligned}\ln\frac{c_\alpha}{c_\beta}&=\text{const}+\frac{x^2}{4D_\alpha t}\left(\frac{D_\alpha}{D_\beta}-1\right)\\&=\text{const}-(\ln c_\alpha)\left(\frac{D_\alpha}{D_\beta}-1\right).\end{aligned} \tag{9}$$

Equation (9) shows that the accuracy of $[(D_\alpha/D_\beta)-1]$ is determined by the accuracy of c_α/c_β and that c_α and c_β must be measured very accurately since $\ln(c_\alpha/c_\beta)$ will change by only about 0.2 across the diffusion zone under the best conditions.

Zinc layers about $\frac{1}{2}\ \mu$ thick, containing Zn^{69} and Zn^{65}, were plated on silver single crystals, grown from 99.999% Ag. The Zn^{69}/Zn^{65} ratio was adjusted so that it was equal to six at the start of counting. Only the gamma-ray peaks from Zn^{65} and Zn^{69} were found in the plated isotopes. The samples were encapsulated, annealed, and sectioned as described elsewhere.[16] The temperatures were controlled and measured to better than ±1°C.

In order to assure a reproducible counting geometry, the sections were dissolved, after weighing, in 1.00 ml of 50% HNO_3. The initial activity of the sections ranged from 10^7 to 5×10^3 cpm. Hot sections were diluted to an activity of 5×10^5 cpm or less, keeping the volume to be counted constant. This was done in order to avoid changes in the gain of the photomultiplier tube and to keep the uncertainty of the dead-time correction to less than 0.1%. Since high-energy gamma rays are being counted, the change in relative absorption due to the dilutions is negligible; this procedure cannot change the isotopic ratio.

The gamma activities of $Zn^{69}(t_{1/2}=13.8\text{ h})$ and $Zn^{65}(t_{1/2}=245\text{ days})$ were separated by half-life. The specific activity of a given section, c, changes with time as

$$c=C_{65}\exp(-\lambda_{65}t)+C_{69}\exp(-\lambda_{69}t), \tag{10}$$

where t is the elapsed time from an arbitrary time zero. Each of the twenty or more sections from a sample were usually counted to 10^6 counts six or more times in

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[11] N. L. Peterson, Phys. Rev. **136**, A568 (1964).

[12] L. W. Barr and A. D. LeClaire, Proc. Brit. Ceram. Soc. **1**, 109 (1964).

[13] N. L. Peterson and L. W. Barr (to be published).

[14] L. W. Barr and J. N. Mundy, *Diffusion in B. C. C. Metals* (American Society for Metals, Metals Park, Ohio, 1965), p. 171.

[15] A. D. LeClaire, Phil. Mag. **7**, 141 (1962).

[16] N. L. Peterson, Phys. Rev. **132**, 2471 (1963).

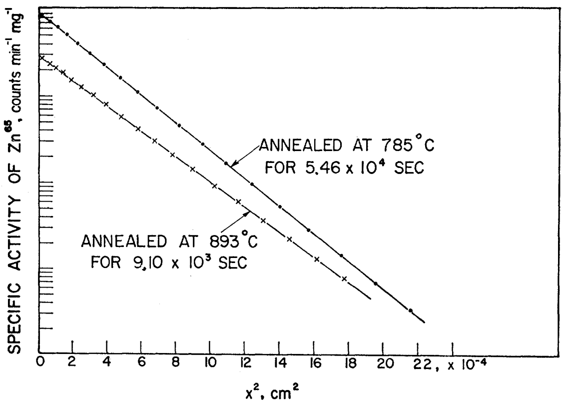

FIG. 1. Log specific activity of Zn^{65} versus penetration distance squared for the diffusion of Zn^{65} in silver.

a period of 5 days; C_{65} and C_{69} were obtained from a linear least-squares fit to Eq. (10). A Cs^{137} source was counted before and after each section in order to correct for long-term counter drifts. The average of three measurements of the decay constant of Zn^{69} gave $\lambda_{69}=(8.380\pm0.015)\times10^{-4}$ min^{-1}, in agreement with the value in the literature.[17] The literature value,[17] 1.9647×10^{-6} min^{-1}, was used for λ_{65}. A well-type scintillation counter was used, and total gamma activity above a lower level was counted. Corrections were made for dead time (1.5 ± 0.1 μsec), background, counter drift, and finite counting time. A null experiment, in which aliquots of different activities taken from the same solution of Zn^{65} and Zn^{69} were counted in the same manner as the sections of a diffusion sample, showed that the isotopic ratios determined by this procedure were not count-rate-dependent.

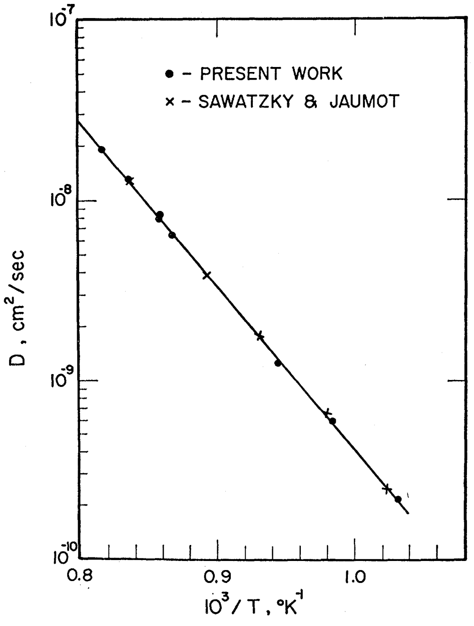

FIG. 2. Log$D$ versus reciprocal absolute temperature for the diffusion of Zn^{65} in silver, showing present data and those of Ref. 18.

The Effect of Zn on the Self- Diffusion of Ag in Dilute Ag-Zn Alloys

Silver-zinc alloys containing 1, 2, 3, and 4 at.% Zn were prepared from 99.999% pure Ag and Zn by induction melting and given a 24 h homogenizing and stress-relief anneal about 30°C below the melting point. The gains after this treatment were several milimeters in diameter. After plating Ag^{110} onto the samples, each sample was sealed into a separate stainless-steel capsule by electron-beam welding to eliminate transport of zinc through the vapor phase. The four stainless-steel capsules plus a pure silver crystal plated with Ag^{110} were sealed off in one quartz capsule and annealed simultaneously so that errors in the time and temperature of the diffusion anneal would not enter into the determination of the relative values of $D_{Ag}(C)$ and $D_{Ag}(0)$. The temperature difference over the five samples was less than 1°C. The stubs of the diffusion samples were analyzed for zinc after sectioning. Errors in $D_{Zn}/D_{Ag}(0)$ were minimized by doing the above diffusion anneals at approximately the same temperature and in the same furnace with the same thermocouples, in which the isotope effect runs were done.

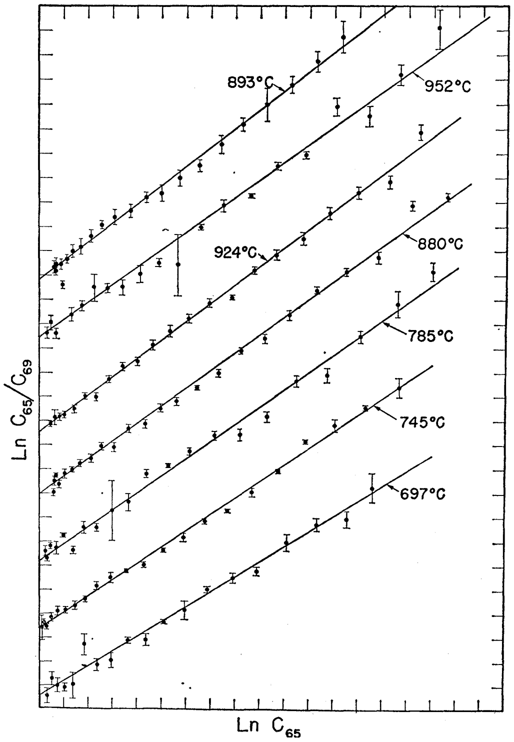

FIG. 3. ln(C_{65}/C_{69}) versus lnC_{65} for the diffusion of zinc in silver. Each division on the ordinate is 0.01. Each division on the abscissa is 0.5; lnC_{65} decreases from left to right.

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[17] Natl. Bur. Std. (U.S.) Circ. 499, 62 (1950).

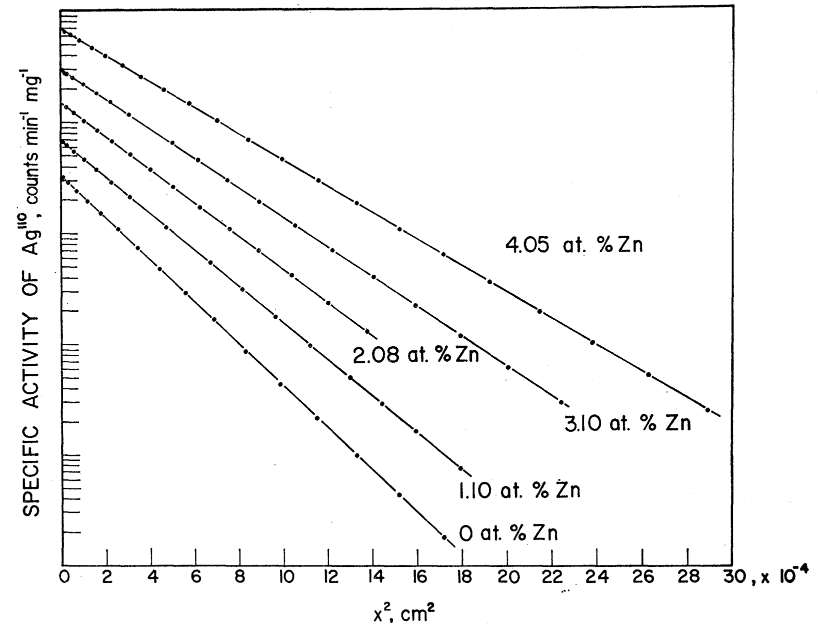

FIG. 4. Log specific activity of Ag^{110} versus penetration distance squared for the diffusion of Ag^{110} in pure silver and silver-zinc alloys.

RESULTS

The Diffusion of Zn^{65} in Silver

Two penetration plots for the diffusion of Zn^{65} in silver are shown in Fig. 1. Their linearity [see Eq. (8)] shows that volume diffusion is being measured, that the dilutions were done accurately, and that zinc loss by evaporation was confined to the first section. The values of D are shown as a function of $1/T$ in Fig. 2 and are listed in Table I. D is given by

$$D=0.532\pm0.006\exp[-(41\,700\pm275)/RT], \quad (11)$$

which agrees with the values of Sawatzky and Jaumot,[18] $D=0.54\exp(-41\,700/RT)$.

Isotope Effect for the Diffusion of Zinc in Silver

Plots of $\ln(C_{65}/C_{69})$ versus $\ln C_{65}$ are shown in Fig. 3. Each division on the ordinate is 0.01; on the abscissa, 0.5. The points are well fitted by straight lines, as expected from Eq. (9). The error bar on each point is the standard error $\ln(C_{65}/C_{69})$ for that section. The values of $(D_{65}/D_{69})-1$ and their standard errors are listed in Table I.

TABLE I. Isotope effect for the diffusion of zinc in silver.

Temp., °C	D, cm²/sec	$(D_{65}/D_{69})-1$	f_i
697	2.15×10^{-10}	0.0125 ± 0.0004	0.48 ± 0.02
745	6.02×10^{-10}	0.0136 ± 0.0002	0.52 ± 0.01
785	1.24×10^{-9}	0.0142 ± 0.0003	0.55 ± 0.01
880	6.39×10^{-9}	0.0148 ± 0.0002	0.57 ± 0.01
893	8.13×10^{-9}	0.0155 ± 0.0002	0.60 ± 0.01
924	1.31×10^{-8}	0.0151 ± 0.0002	0.58 ± 0.01
952	1.98×10^{-8}	0.0146 ± 0.0004	0.56 ± 0.02

Effect of Zn on the Diffusion of Ag in Ag-Zn Alloys

Penetration plots for the diffusion of Ag^{110} in Ag-Zn alloys at 747°C are given in Fig. 4. The values of D from this run and from the run at 880°C are plotted versus zinc concentration in Fig. 5 and given in Table II, which also gives the values of b [Eq. (6)]. The value of D_{Ag} from the 4% Zn alloy at 747°C has been omitted from the determination of b; solute-solute interactions are apparently significant at this temperature and concentration. The values of $D_{Ag}(0)$ agree with those of Tomizuka and Sonder.[19]

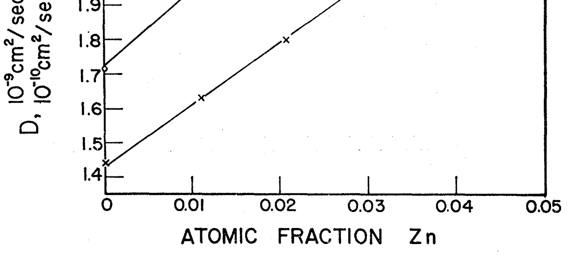

FIG. 5. Diffusion coefficient of silver in silver-zinc alloys versus zinc concentration for diffusion at 747 and 880°C.

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[18] A. Sawatzky and F. E. Jaumot, Phys. Rev. **100**, 1627 (1955).

[19] C. T. Tomizuka and E. Sonder, Phys. Rev. **103**, 1182 (1956).

TABLE II. Effect of zinc on self-diffusion in silver.

C_{Zn}, at.%	747°C D, 10^{-10} cm²/sec	880°C D, 10^{-9} cm²/sec
0	1.43	1.72
1.10	1.63	1.99
2.08	1.80	2.18
3.10	2.00	2.41
4.05	2.28	2.62
	$b=12.6$	$b=12.7$
	$f_i=0.53$	$f_i=0.61$

The Correlation Factors

The correlation factors for the diffusion ot zinc in silver, obtained from the isotope effect by means of Eq. (5) (and $\Delta K=0.86$),[13] are given in Table I and plotted versus $1/T$ in Fig. 6. The correlation factors obtained from the effect of zinc on the diffusion of silver by means of the Lidiard theory [Eq. (6) and (7)] are also plotted in Fig. 6 and given in Table II.

Errors

The errors in values of D are estimated to be 1%; the agreement with other workers is usually within 2%. This leads to an error of 4% in f_i determined by the Lidiard and Howard-Manning theories. The standard errors in $(D_{65}/D_{69})-1$, derived from the least-squares analysis of the lines in Fig. 3, are about 3%. The error in f_i determined from the isotope effect is the same, neglecting possible errors in ΔK.

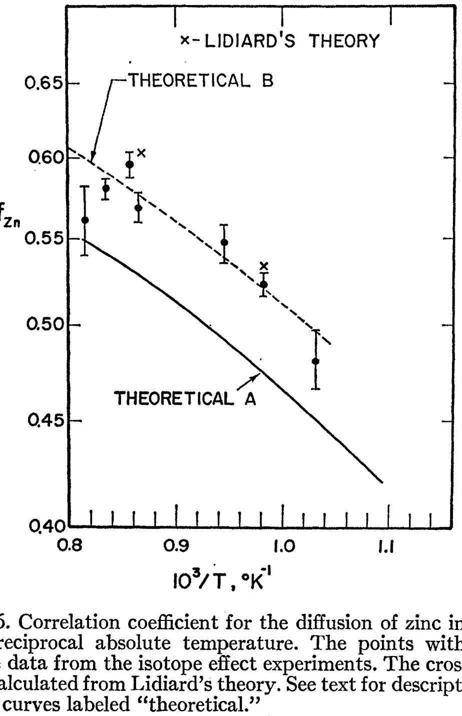

FIG. 6. Correlation coefficient for the diffusion of zinc in silver versus reciprocal absolute temperature. The points with error bars are data from the isotope effect experiments. The crosses are values calculated from Lidiard's theory. See text for descriptions of the two curves labeled "theoretical."

The error bars on $\ln(C_{65}/C_{69})$ are usually less than 0.003, although some are larger. These error bars include all the random errors in the counting. Such effects as incorrect sample volume, absorption differences due to extra thick or thin glass bottles, or slight amounts of contamination are probably responsible for points lying off the least-squares line by more than the length of the error bar. The standard deviation of $\ln(C_{65}/C_{69})$ from the null experiment is about the same as the deviations in a regular run, thus indicating that any systematic error resulting from the counting procedure is very small. Changing the counter dead time by 0.25 μsec, the decay constant of Zn^{69} by 0.04×10^{-4} min^{-1}, or leaving the counter drift correction out changed $[(D_{65}/D_{69})-1]$ by less than 2%. The general self-consistency of the data indicates that serious systematic errors are probably absent.

DISCUSSION

Comparison with LeClaire's and Lidiard's Theories

f_i is calculated from LeClaire's theory[5] by first calculating ΔH_j, the difference between the activation energies for w_j and w_0 jumps,

$$\frac{w_j}{w_0}=\frac{\nu_j}{\nu_0}\exp\left(-\frac{\Delta H_j}{RT}\right) \tag{12}$$

from the screened electrostatic interaction between the impurity and the vacancy. Taking $\nu_1=\nu_3=\nu_0$ and the theoretical values of ν_2/ν_0 and ΔH_j, one calculates f_i as a function of T from Eqs. (12) and (1). The results are plotted as the Theoretical A curve in Fig. 6; the agreement with experiment is quite good.

We have extended this calculation to include association jumps by calculating ΔH_4 ($\Delta H_4=-0.51$ kcal/mole at $RT=2$ kcal/mole) on the lines of LcClaire's model, assuming $(\nu_4/\nu_0)=1$, and using Eq. (1a) for f_i. This yields values of f_i about 0.75 as large as LcClaire's with much the same temperature dependence. The f_i calculated from our values of b by means of Lidiard's theory are also in good agreement with the f_i from the isotope effect.

The Jump-Frequency Ratios

Howard and Manning[6] have calculated f_i for various values of w_4/w_0 using our values of b and $D_i/D_S(0)$ at 747 and 880°C. The results of this calculation, which gave values of f_i in agreement with the isotope effect experiments, are as follows.

T°C	w_4/w_0	w_3/w_1	w_2/w_1	f_i
747	1.15	0.27	1.53	0.525
880	1.3	0.39	1.54	0.567

Since a change of 0.1 in w_4/w_0 changes the calculated f_i by only 4%, the temperature dependence of these jump-frequency ratios cannot be deduced from the above values. However, a self-consistent set of jump frequencies, as a function of temperature, can be obtained by combining the above results with the ΔH_j's calculated by LeClaire. Taking $w_4/w_0=1.15$ at 747°C and $\Delta H_4=-0.510$ kcal/mole, we have calculated w_4/w_0 as a function of temperature. We next calculated w_2/w_3 from the formula[20]

$$\frac{D_i}{D_s(0)}=\frac{f_i w_4 w_2}{f_0 w_0 w_3}, \tag{13}$$

using Tomizuka's and Sonder's[19] values of $D_S(0)$, and our values of D_i, f_i, and w_4/w_0. w_2/w_1 and w_3/w_1 were then determined from the experimental values of f_i, the above values of w_2/w_3, Eq. (1a) and the values of F deduced from the values of w_4/w_0 (case I). The calculation was then repeated for the three cases (II) $w_4/w_0=1.3$ at 880°C and $\Delta H_4=-0.510$ kcal/mole, (III) $w_3/w_1=0.27$ at 747°C and $\Delta H_3-\Delta H_1=-0.190$ kcal/mole (this was calculated by LeClaire) and (IV) $w_3/w_1=0.39$ at 880°C and $\Delta H_3-\Delta H_1=-0.190$ kcal/mole. The values of w_4/w_0, w_2/w_3, w_2/w_1, and w_3/w_1 for case IV are plotted versus $1/T$ in Fig. 7. The lines on Fig. 7 have been drawn so that the slopes are equal to $\Delta H_j/R$, where the values of ΔH_j are those calculated by LeClaire. Essentially identical lines were obtained for all four cases. The ratios of the ν's for the four cases agree within ±10%; the average values are $\nu_4/\nu_0=0.99$, $\nu_3/\nu_1=0.31$, $\nu_2/\nu_3=0.82$ and $\nu_2/\nu_1=0.24$. These ν ratios, LeClaire's values of ΔH_j and Eq. (1a) were then used to to calculate f_i as a function of temperature. The result is the "Theoretical B" curve of Fig. 6. The f_i's, calculated using the ν ratios for the four cases, were the same within 0.3%. It should be noted that; since the temperature dependence of w_4/w_0 and w_3/w_1 is small, these ν ratios are almost entirely based on experimental data.

The ratio ν_2/ν_0 may be calculated from the expression[15]

$$\frac{\nu_2}{\nu_0}=\frac{D_{i0}}{D_{s0}(0)}\frac{f_0}{f_i}\exp(C/RT), \tag{14}$$

where D_{i0} and $D_{S0}(0)$ are the pre-exponentials in the Arrhenius equations for D_i and $D_S(0)$, f_0 is the correlation factor for self-diffusion ($f_0=0.7815$ for an fcc lattice) and

$$C=R\frac{\partial \ln f_i}{\partial 1/T}.$$

Using LeClaire's value of C, which adequately describes our data, and the experimental values of D_{i0}, $D_{S0}(0)$, and f_i, we obtain $(\nu_2/\nu_0)=0.70$. Combining this with the average ν ratios, we get $(\nu_1/\nu_0)=2.9$, $(\nu_3/\nu_0)=0.90$, and $(\nu_4/\nu_0)=0.99$.

The experimental values of f_i are closer to the theoretical curve B than to the theoretical curve A. The main difference between the two theoretical curves is in the ν ratios used to calculate f_i; this indicates that, for zinc diffusing in silver, LeClaire's theory gives good values of the ΔH_j, and that the assumption of $\nu_1=\nu_0$ is not valid. Although the slopes of the lines on Fig. 7, from which the ν ratios were determined, could be changed somewhat, lines drawn to give intercepts that give $\nu_1=\nu_0$ do not fit the points at all.[20a]

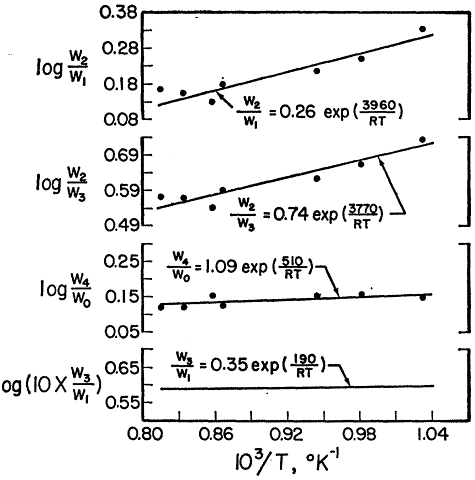

FIG. 7. Jump frequency ratios versus reciprocal absolute temperature.

The Influence of ΔK on f_i

The experimental values of f_i were calculated from the isotope effect using Peterson's and Barr's value of ΔK[13] (measured at 930°C) and two assumptions: first, that ΔK is independent of temperature, and second, that ΔK is the same for zinc diffusing in silver as it is for silver self-diffusion. That ΔK may be temperature-dependent is indicated by the drop in f_i above 900°C (Fig. 6). This may not be a drop in f_i but a drop in ΔK, or it may be experimental error.

We estimate that ΔK for the diffusion of Zn in Ag is within a few percent of that for self-diffusion, for the following reason. A correlation exists between ΔK and ΔV^*, the ratio of the activation volume for diffusion to the molar volume.[14] Since ΔV^* changes by 5% on going from Ag to In,[21] ΔV^*, and therefore ΔK for Zn diffusing in Ag, should differ from the value for self-diffusion by no more than 3%.

The assumption that only ν_2 depends on the mass of the diffusing isotope is also not rigorously correct if

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[20] R. E. Howard and A. B. Lidiard, Rept. Progr. Phys. **27**, 161 (1964), or Ref. 6.

[20a] *Note added in proof.* It should be noted that this is a self-consistent set of values for ν_i and ΔH_i, but not a unique set. Manning (private communication) pointed out that appreciably different values of ΔH_4 will fit the data almost as well as that in Fig. 7 but will give appreciably different values of ν_i and ΔH_i than those in Fig. 7.

[21] F. R. Bonanno and C. T. Tomizuka, Phys. Rev. **137**, A1264 (1965).

$\Delta K<1$.[8] However, using the formulas derived by LeClaire, we find that this would change f_i by no more than 3%. A small, temperature-independent change in ΔK will cause a similar change in the calculated values of ν_3/ν_0.

SUMMARY

The correlation factor for the diffusion of zinc in silver has been obtained from measurements of the isotope effect. b has also been determined for this system. The values of f_i and b are consistent with the predictions of Howard and Manning. Good agreement with Lidiard's and LeCaire's theories is also obtained; the latter is improved by taking into account the dissociation jumps and calculating the ratios of the vibration frequencies from the experimental data by means of Howard's and Manning's equations. The good agreement between the experimental data and the existing theories of impurity diffusion suggests that the model which neglects vacancy-impurity interactions beyond the second nearest-neighbor position is correct within experimental accuracy.

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Isotope Effect for the Diffusion of Zinc in Copper, and Ordered and Disordered CuZn†

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The strength of the isotope effect for the diffusion of zinc in copper is 0.41 at 894.5 and 946.4°C. The most probable value of the correlation factor for the diffusion of zinc in copper is 0.55. The strength of the isotope effect for the diffusion of zinc in disordered CuZn at 560.3°C is 0.245; it is 0.201 for diffusion in ordered CuZn at 410.6°C ($S=0.7$). The near equality of these numbers indicates that next-nearest-neighbor jumps are not probable, that the details of the diffusion mechanism are the same in the ordered and disordered phases, and that at this degree of long-range order, the Elcock-McCombie mechanism is not dominant.

INTRODUCTION

In a previous paper,[1] we described isotope effect measurements for the diffusion of zinc in silver. The present paper reports similar measurements for zinc diffusion in copper and ordered and disordered CuZn. The correlation factor for the diffusion of zinc in silver was obtained fairly exactly from the isotope effect[1]; the same cannot be done for copper and CuZn, for the following reasons.

The relation between the strength of the isotope effect E and the correlation factor is given by

$$E\equiv\frac{(D_\alpha/D_\beta-1)}{(m_\beta/m_\alpha)^{1/2}-1}=f_i\Delta K, \qquad (1)$$

where D_α and D_β are the diffusion coefficients of two isotopes of the same element of masses m_α and m_β, f_i is the correlation factor, and ΔK is the fraction of the translational kinetic energy, associated with motion in the jump direction, that is possessed by the jumping atom at the saddle point.[2] Since ΔK is not known for copper only an approximate value of f_i can be obtained from E.

Equation (1) was derived for systems having at least twofold rotational symmetry about the jump direction.[3] Such conditions are not met in a disordered concentrated alloy, and it is not clear that Eq. (1) is valid for an ordered alloy. However, an isotope effect experiment for zinc diffusion in CuZn can give some qualitative information concerning the mechanism of atomic jumps. If diffusion in ordered CuZn takes place by next-nearest-neighbor jumps, i.e., if zinc diffused exclusively on the simple cubic zinc lattice, Eq. (1) would apply, with $f=0.655$.[4] If diffusion in the disordered alloy takes place by jumps with the ordinary Bardeen-Herring correlation and diffusion in the

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[1] S. J. Rothman and N. L. Peterson, preceding paper, Phys. Rev. **154**, 552 (1967).

[2] J. G. Mullen, Phys. Rev. **121**, 1649 (1961).

[3] K. Tharmalingam and A. B. Lidiard, Phil. Mag. 4, 899 (1959).

[4] K. Compaan and Y. Haven, Trans. Faraday Soc. **54**, 1498 (1958).