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Screened Interaction Model for Impurity Diffusion in Zinc*†

P. B. GHATE‡
Rensselaer Polytechnic Institute, Troy, New York

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The screening theory proposed by Lazarus has been used to examine the impurity diffusion in zinc. The difference in the activation energies (ΔQ) for the impurity diffusion and self-diffusion in zinc have been calculated using a screened Coulomb interaction between the vacancy and the excess charge Ze of the impurity ion. The change in the energy of formation of a vacancy next to the impurity ion is calculated by considering the electrostatic interaction between the impurity ion and the vacancy when they are nearest neighbors. In a saddle-point configuration, the diffusion ion may be assumed to be flanked by two half-vacancies. The change in the energy of motion has been calculated by considering the electrostatic interaction between the two half-vacancies and the impurity ion in the saddle-point configuration. Correlation corrections have been calculated using the expressions for the correlation factors. The estimated differences in activation energies for trivalent and monovalent impurities in zinc have been compared with the available experimental data. The estimated values check fairly well in the case of indium and gold, whereas the agreement is poor in the case of silver. Correlation corrections are important for a trivalent impurity, whereas the diffusional jumps of the monovalent impurity are relatively uncorrelated.

INTRODUCTION

SINCE the tracers became readily available, a considerable amount of experimental data on tracer diffusion in metallic systems has been accumulating. It is known that impurities diffuse at a different rate with different activation energies and frequency factors as compared to self-diffusion. The screening theory proposed by Lazarus[1] has been fairly successful in accounting for the impurity diffusion in monovalent metals. According to this theory the change in the activation energy is taken to be made up of two parts: the change in the energy of formation of a vacancy next to the impurity ion and the change in the energy of motion. Size effects and correlation corrections have been completely ignored. On the other hand, Swalin[2] has taken a different point of view. He has calculated the difference in activation energies from purely elastic considerations and the main emphasis is on size effects. However, the impurity diffusion data tend to show a systematic trend as a function of the valence of the diffusing ion. LeClaire[3] has used the screened interaction model with considerable success to account for the impurity diffusion in copper, silver, and gold. He has included the correlation corrections, whereas the size effects have been neglected. Recently, experimental data on impurity diffusion in a noncubic divalent metal zinc have been reported.[4,5] Self-diffusion data on zinc are also available[6] (see Table I). It is the purpose of the present article to apply the screened interaction model to the understanding of the impurity diffusion in zinc and to examine to what extent the simple model is valid for a hexagonal matrix. The main emphasis, however, is on calculating the differences in the activation energies (ΔQ) for self-diffusion and impurity diffusion and on checking these calculations against the experimental values.

TABLE I. Frequency factors and activation energy for tracer diffusion in zinc single crystals.

Isotope	Diffusion direction	Frequency factors (cm²/sec)	Activation energy (kcal/mole)	Ref.
In^{114}	‖	0.062±0.008	19.1±0.1	4
In^{114}	⊥	0.14 ±0.02	19.6±0.1	4
Ag^{110}	‖	0.32 ±0.02	26.0±0.1	4
Ag^{110}	⊥	0.45 ±0.07	27.6±0.2	4
Au^{198}	‖	0.97 ±0.22	29.7±0.3	5
Au^{198}	⊥	0.29 ±0.12	29.7±0.5	5
Zn^{65}	‖	0.13	21.8±0.2	6
Zn^{65}	⊥	0.58	24.3±0.5	6

DIFFERENCE IN THE ACTIVATION ENERGY: ΔQ

The method of calculating ΔQ is illustrated for the impurity diffusion in the parallel direction. (Parallel direction and also c axis will always mean the direction parallel to the hexagonal axis.) Experiments indicate that the diffusion coefficients for zinc tracer and impurity can be expressed by simple Arrhenius-type equations:

$$D_{\|,0}=A_{\|,0}\exp(-Q_{\|,0}/RT), \tag{1}$$

$$D_{\|}=A_{\|}\exp(-Q_{\|}/RT). \tag{2}$$

$D_{\|,0}$ and $D_{\|}$ are the corresponding diffusion coefficients

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[†] Work supported by the U. S. Atomic Energy Commission.

[‡] Present address: Department of Engineering Physics and Materials Science, Cornell University, Ithaca, New York.

[1] D. Lazarus, Phys. Rev. **93**, 973 (1954); *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1960), Vol. 10.

[2] R. A. Swalin, Acta Met. **5**, 443 (1957).

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

[4] J. H. Rosolowski, Phys. Rev. **124**, 1828 (1961).

[5] P. B. Ghate, Phys. Rev. **131**, 174 (1963).

[6] G. A. Shirn, E. S. Wajda, and H. B. Huntington, Acta Met. **1**, 513 (1953).

of zinc tracer and impurity parallel to the c axis in zinc single crystals. $Q_{||,0}$ and $Q_{||}$ are the corresponding activation energies for zinc tracer and impurity expressed in calories/mole. $A_{||,0}$ and $A_{||}$ are the frequency factors.

From the atomistic point of view, we can express $D_{||,0}$ and $D_{||}$ as

$$D_{||,0}=\tfrac{1}{16}c^2\nu_{A0}f_{A,z:0}\exp(\delta S_{A0}/R) \times\exp[-(E_{A0}+H_{A0})/RT], \quad (3)$$

$$D_{||}=\tfrac{1}{16}c^2\nu_{A}f_{A,z}\exp(\delta S_{A}/R) \times\exp[-(E_{A}+H_{A})/RT], \quad (4)$$

where ν_{A0} and ν_A are the corresponding nonbasal (or abasal) frequencies for zinc and impurity atoms, $f_{A,z:0}$ and $f_{A,z}$ are the correlation factors for self-diffusion and impurity diffusion in the parallel direction, E_{A0} and E_A are the energies of formation of a vacancy next to zinc and impurity in solvent metal, H_{A0} and H_A are the activation energies for exchange of a zinc atom with the vacancy and that of an impurity atom with the vacancy, and δS_{A0} and δS_A are the entropy factors in both cases.

To a first approximation, we assume that δS_{A0} and δS_A are equal. (In the case of self-diffusion, no distinction is made between the tracer atom and zinc atom in the host lattice.) The correlation factors are temperature-dependent, and hence the activation energy measured in an experiment may not be identified as equal to $E_{A0}+H_{A0}$ or E_A+H_A, as the case may be. From the experimental data, one usually finds $-R\partial \ln D/\partial(1/T)$ and identifies it with the activation energy. Expressions (4) and (3) can be treated in a similar manner. Then we get

$$-R[\partial \ln D/\partial(1/T)]=H_A+E_A-R[\partial \ln f_{A,z}/\partial(1/T)],$$

$$Q_{||}=H_A+E_A-C_A.$$

Similarly,

$$Q_{||,0}=H_{A0}+E_{A0}-C_{A0}.$$

Therefore,

$$Q_{||}-Q_{||,0}=(H_A-H_{A0})+(E_A-E_{A0})-(C_A-C_{A0}) \quad (5)$$

$$\Delta Q_{||}=\Delta H_A+\Delta E_A-\Delta C_A.$$

If ΔE_A is negative, vacancies are attracted by impurity ion; and if positive, repelled by them. The quantity $(-\Delta E_A)$ is then the binding energy between the impurity and a vacancy. We shall assume that many of the factors contributing to the absolute value of the activation energy (and frequency factor) to be nearly the same for both solute and solvent. As mentioned earlier, our main attempt will be to account for $\Delta Q_{||}=Q_{||}-Q_{||,0}$ rather than trying to calculate $Q_{||}$ and $Q_{||,0}$ directly.

SCREENED INTERACTION MODEL TO CALCULATE ΔQ

We assume a free-electron model for the solvent and that both the valence electrons can be treated as free. The positive charge of the doubly ionized zinc ions is smeared out uniformly. A vacancy in zinc metal will be treated as a point charge $-2e$. Whenever an impurity of different valence is dissolved substitutionally in zinc matrix, we shall assume that the impurity ion can be treated as a point charge Ze. For indium and silver (or gold) as solutes in zinc, Z will be $+1$ and -1, respectively. This excess charge attracts electrons (if Z is positive) or holes (if Z is negative) to screen the charge at large distances. The potential $V(r)$ around the impurity ion is calculated in the linearized Thomas-Fermi approximation.[7] Then,

$$V(r)=(Ze/r)\exp(-qr), \quad (6)$$

where $q^2=(4me^2/\hbar^2)(3n_0/\pi)^{1/3}$, m is the mass of an electron, e is the electronic charge, n_0 is the number of electrons per unit volume, $\hbar$ is Planck's constant divided by 2π, and q is the screening constant. Lattice parameters[8] $a=2.66$ Å and $c=4.94$ Å were used to calculate n_0 and, hence, q. We get $n_0=1.321\times10^{23}$ electrons/cc and $q=1.947\times10^8$ cm^{-1}.

Recently, solutions of the Thomas-Fermi equation have been given in a series form for monovalent metals.[9–11] The leading term is, for V, at a distance r from the excess point charge,

$$V(r)=\alpha(Ze/r)\exp(-qr). \quad (7)$$

The values of α have been listed for different Z values. No such solutions are available for a divalent metal zinc. The "master solution" given by Umeda and Koboyashi[10] has been used to obtain α for $Z=+1$ in zinc by interpolation. The value of α turns out to be 0.83. For impurities with negative Z, the method suggested by Alfred and March[11] has been used to evaluate α for $Z=-1$. This turns out to be 1.3. Diffusion of indium, silver, and gold is considered in detail. Before we proceed to calculate ΔQ, a brief review on the correlation factors[12] for the zinc lattice is now given.

CORRELATION FACTORS

The expression for the correlation factor[12–14] can be written as

$$f_{i,j}=1+2\sum_{n=1}^{\infty}\frac{\boldsymbol{\lambda}_{i,j}\cdot\boldsymbol{\lambda}_{n(i)}}{(\lambda_{i,j})^2}, \quad (8)$$

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[7] N. F. Mott, Proc. Cambridge Phil. Soc. **32**, 281 (1936).

[8] C. Kittel, *Introduction to Solid State Physics* (John Wiley & Sons, Inc., New York, 1953), 2nd ed., p. 41.

[9] H. Fujiwara, J. Phys. Soc. Japan **10**, 339 (1955); **13**, 250 (1958); **13**, 939 (1958).

[10] K. Umeda and S. Kobayshi, J. Phys. Soc. Japan **13**, 148 (1958).

[11] L. C. R. Alfred and N. H. March, Phil. Mag. (7) **46**, 759 (1955); Phys. Rev. **103**, 877 (1956); Phil. Mag. (7) **48**, 985 (1957).

[12] H. B. Huntington and P. B. Ghate, Phys. Rev. Letters **8**, 421 (1962).

[13] J. G. Mullen, Phys. Rev. **124**, 1723 (1961); Phys. Rev. Letters **9**, 383 (1962); (private communication).

[14] The possibility of some numerical errors in the equations in Ref. (12) was suggested to us by Dr. A. D. LeClaire. The numerical errors have been corrected and the correct equations are given in this article. The suggestion of Dr. A. D. LeClaire is gratefully acknowledged.

[15] A. D. LeClaire and A. B. Lidiard, Phil. Mag. **B1**, 518 (1956).

where $\boldsymbol{\lambda}_{i,j}$ is the jth component of the ith-type jump and $\boldsymbol{\lambda}_{n(i)}$ is the nth jump of the diffusion atom in the sequence of the jumps of the diffusing atom that followed ith type in question. We introduce the vector

$$\mathbf{S}_i=\sum_{n=1}^{\infty}\boldsymbol{\lambda}_{n(i)}\,, \tag{9}$$

which can be thought of as representing the average final displacement of the tracer. One can solve for the $\mathbf{S}_i$ by a sort of recursion relation. Suppose the various jump rates of the vacancy are given by ω_m, where the particular ω_r represents the reverse impurity vacancy jump. Then

$$\mathbf{S}_i=\left(\textstyle\sum_m \omega_m \mathbf{S}_m-\omega_r\boldsymbol{\lambda}_i\right)/\textstyle\sum_m \omega_m\,. \tag{10}$$

$f_{i,j}$ can then be expressed as

$$f_{i,j}=1+2\mathbf{S}_i\cdot\mathbf{j}/(\lambda_{i,j})\,, \tag{11}$$

where $\mathbf{j}$ is the unit vector in the jth direction.

The expressions for the vectors $\mathbf{S}_i$ and the correlation factors are now evaluated. Let the z axis be parallel to the hexagonal axis. For a vacancy site B adjoining the diffusing impurity atom and in the same basal plane, the following frequencies are pertinent (see Fig. 1): ω_a, jump of B to another neighboring site in adjoining basal plane; ω_b, jump of B to a neighboring site in the same basal plane; ω_c, jump of B to a site which does not adjoin the diffusing atom; and ω_B, exchange of diffusing atom with the vacancy in the same basal plane.

For a vacancy site A adjoining the impurity but in a different basal plane, the following frequencies are pertinent: ω_a', jump of A into the same basal plane as that of the diffusing atom; ω_b', jump of A to another A site; ω_c', jump of A to a site which does not adjoin the diffusing atom; ω_A', exchange of the diffusing atom with the vacancy at site A.

There are two different kinds of jump lengths for the diffusing atom in the hexagonal lattice λ_A [jump length of nonbasal (abasal) jump] and λ_B (jump length of basal jump), depending on the initial position of the vacancy.

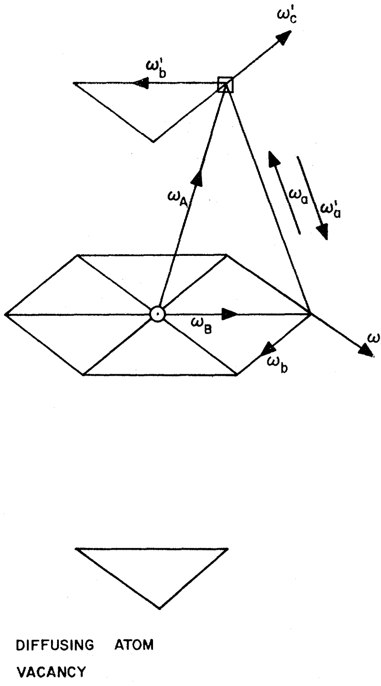

FIG. 1. Nearest neighbors of a diffusing ion and the pertinent frequencies.

For $\mathbf{S}_A$, the suitable resolution is into components $S_{A,z}$ and $S_{A,b}$, respectively, parallel to the hexagonal axis and the projection of λ_A on the basal plane. The appropriate components of $\mathbf{S}_B$ are $S_{B,x}$ and $S_{B,y}$. The x axis is so chosen that it coincides with the jump length λ_B.

We have, from Eq. (10), for the z component

$$S_{A,z}=\frac{-\omega_A(S_{A,z}+1)}{2\omega_a'+7F\omega_c'+\omega_A}\,, \tag{12}$$

$$f_{A,z}=\frac{2\omega_a'+7F\omega_c'}{2\omega_a'+2\omega_A+7F\omega_c'}\,. \tag{13}$$

For the diffusion in the basal plane,

$$S_{A,b}=\frac{2\omega_a'[(\sqrt{3}/2)S_{B,x}+\frac{1}{2}S_{B,y}]+2\omega_b'(-\frac{1}{2})S_{A,b}-\omega_A(\lambda_{A,b}+S_{A,b})}{2\omega_a'+2\omega_b'+7F\omega_c'+\omega_A}\,, \tag{14}$$

$$S_{B,x}=\frac{2\omega_a(\sqrt{3}/2)S_{A,b}+2\omega_b(\frac{1}{2})S_{B,x}-\omega_B(\lambda_B+S_{B,x})}{2\omega_a+2\omega_b+7F\omega_c+\omega_B}\,, \tag{15}$$

$$S_{B,y}=\frac{2\omega_a(\frac{1}{2})S_{A,b}+2\omega_b(-\frac{1}{2})S_{B,y}}{2\omega_a+2\omega_b+7F\omega_c+\omega_B}\,. \tag{16}$$

After solving the set of linear equations (14), (15), and (16) for $S_{A,b}$ and $S_{B,x}$ one can substitute the results into Eq. (11). Then,

$$f_{A,b}=1+2S_{A,b}/\lambda_{A,b} \tag{17}$$

and

$$f_{B,x}=1+2S_{B,x}/\lambda_B\,. \tag{18}$$

The escape jump rates $7\omega_c$ and $7\omega_c'$ have been multiplied by a factor F. In the LeClaire–Lidiard[15] approximation $F=1$, and this corresponds to the case where a vacancy jumping away to a nonnearest-neighbor position is assumed to be completely dissociated from the impurity atom. The effect of the vacancies returning

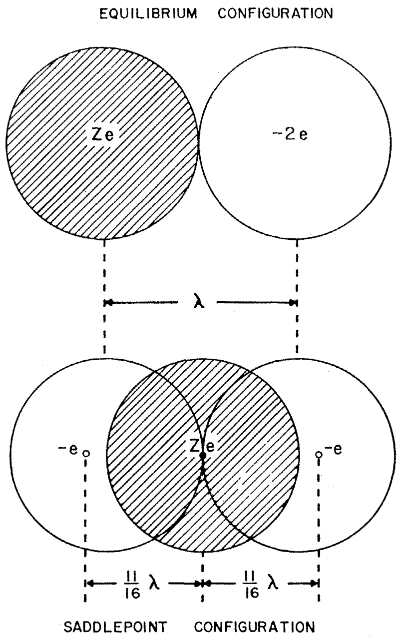

FIG. 2. Diffusing ion and the vacancy in the equilibrium configuration and in saddle-point configuration.

back to the nearest-neighbor positions is to reduce the values of $7\omega_c$ and $7\omega_c'$. In the case of an fcc lattice, the effect of returning vacancies on the correlation factor has been worked out by Manning,[16] and F is approximately equal to 0.736. In the case of hexagonal structures, F can, approximately, be set equal to 0.736.[17] This seems to be a good choice, as the correlation factors reduce to 0.78 within a fraction of a percent when all frequencies are equal. The correlation factors for hexagonal structure have been obtained by Compaan and Haven[18] and Mullen[13] by different techniques, and they obtain a value close to 0.78, within a fraction of a percent, when all the frequencies are equal. With $F=0.736$, the equations for $f_{A,z}$, $f_{A,b}$, and $f_{B,z}$ are used in evaluating the correlation correction.

IMPURITY DIFFUSION IN THE PARALLEL DIRECTION

It has been shown earlier that $\Delta Q_{\parallel}$ is made up of three parts, namely, ΔE_A, ΔH_A, and ΔC_A. These quantities are calculated as follows:

ΔE_A. A vacancy in a divalent metal zinc is treated as a point charge $-2e$. The change in the energy of formation ΔE_A is assumed to be due mainly to the electrostatic interaction between the vacancy and the impurity ion when they are nearest neighbors. Since we are interested in the parallel diffusion, the vacancy and the impurity are in the adjacent planes. The nearest-neighbor distance (nonbasal jump distance) is equal to λ_A (see Fig. 2). Then,

$$\Delta E_A = -2eV(\lambda_A). \qquad (19)$$

$V(r)$ is given by Eq. (7). For indium we set $Z=+1$ and $\alpha=0.83$, and for silver (or gold) $Z=-1$ and $\alpha=1.3$. The values of ΔE_A are listed in Table II. This model has been used earlier by Lazarus[1] and LeClaire[3] for impurity diffusion in monovalent metals with a considerable amount of success.

ΔH_A. For the saddle-point configuration, we assume that the diffusing ion, situated midway between two equilibrium sites, is flanked by two half-vacancies whose charges are assumed to be centered at the centroids of the hemispheres (see Fig. 2). (This simple model was suggested earlier by Huntington[19] and has been employed recently by LeClaire[3] with fair success.) Then, ΔH_A is estimated as the difference in electrostatic-interaction energies between the two charges $-e$, each situated at a distance $(11/16)\lambda_A$ from the impurity ion of effective charge Ze, and a charge $-2e$ situated at a distance λ_A from the impurity ion. We get,

$$\Delta H_A = -2eV(11\lambda_A/16) - \Delta E_A.$$

Therefore,

$$\Delta E_A + \Delta H_A = -2eV(11\lambda_A/16). \qquad (20)$$

The values of ΔH_A are listed in Table II for indium, silver, and gold.

ΔC_A. The expression for $f_{A,z}$ developed earlier will now be used to calculate the correlation correction. Let

$$\begin{aligned} \omega_a' &= \nu_a' \exp(-H_a'/RT), \\ \omega_A' &= \nu_A \exp(-H_A/RT), \qquad (21) \\ \omega_c' &= \nu_c' \exp(-H_c'/RT), \end{aligned}$$

where ν_a', ν_A, and ν_c' are the appropriate frequencies and H_a', H_A, and H_c' are the appropriate activation energies. Then,

$$f_{A,z} = \frac{\nu_a' \exp(-H_a'/RT) + \frac{7}{2}F\nu_c' \exp(-H_c'/RT)}{\nu_a' \exp(-H_a'/RT) + \nu_A \exp(-H_A/RT) + \frac{7}{2}F\nu_c' \exp(-H_c'/RT)},$$

[see Eq. (13)]. Divide the numerator and the denominator by ω_{A0}, where $\omega_{A0} = \nu_{A0} \exp(-H_{A0}/RT)$ represents

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[16] J. R. Manning, Phys. Rev. Letters **1**, 365 (1958); Phys. Rev. **116**, 819 (1959); H. B. Huntington (private communication); Phys. Rev. **128**, 2169 (1962).

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

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

[19] H. B. Huntington, Phys. Rev. **61**, 325 (1942).

the nonbasal jump probability of the zinc atom in the lattice. Then,

$$f_{A,z}=\frac{(\nu_a'/\nu_{A0})\exp(-\Delta H_a'/RT)+\frac{7}{2}F(\nu_c'/\nu_{A0})\exp(-\Delta H_c'/RT)}{(\nu_a'/\nu_{A0})\exp(-\Delta H_a'/RT)+(\nu_A/\nu_{A0})\exp(-\Delta H_A/RT)+\frac{7}{2}F(\nu_c/\nu_{A0})\exp(-\Delta H_c'/RT)},$$

$\Delta H_a'=H_a'-H_{A0}$, and so on.

Since ν_a', ν_c', and ν_{A0} refer to the frequencies of the same atomic species, we may assume with Manning[16] that the ratios ν_a'/ν_{A0} and ν_c'/ν_{A0} can be set equal to unity. A minor point that may be noted here is that $7\omega_c'$ actually involves nonbasal and basal escape jumps. Since the effect of this quantity on ΔC_A is small, as the numbers will indicate later, setting $\nu_c'/\nu_{A0}=1$ is not a serious approximation. Therefore,

$$f_{A,z}=\frac{\exp(-\Delta H_a'/RT)+\frac{7}{2}F\exp(-\Delta H_c'/RT)}{\exp(-\Delta H_a'/RT)+(\nu_A/\nu_{A0})\exp(-\Delta H_A/RT)+\frac{7}{2}F\exp(-\Delta H_c'/RT)}. \tag{22}$$

We can use this expression to evaluate $\partial\ln(f_{A,z})/\partial(1/T)$. A long but straightforward calculation gives

$$C_A=\frac{(\Delta H_A-\Delta H_a')\exp\left[-\dfrac{\Delta H_A+\Delta H_a'}{RT}\right]+\frac{7}{2}F(\Delta H_A-\Delta H_c')\exp\left[-\dfrac{\Delta H_A+\Delta H_c'}{RT}\right]}{[\exp(-\Delta H_a'/RT)+\frac{7}{2}F\exp(-\Delta H_c'/RT)]^2}\frac{A_{\parallel}}{A_{\parallel,0}}f_{A,z:0}\exp\frac{\Delta C_A}{RT}. \tag{23}$$

We also note that

$$\frac{\nu_A}{\nu_{A0}}=\frac{A_{\parallel}}{A_{\parallel,0}}\frac{f_{A,z:0}}{f_{A,z}}\exp\frac{\Delta C_A}{RT} \tag{24}$$

and

$$f_{A,z}=1-\frac{A_{\parallel}}{A_{\parallel,0}}f_{A,z:0}\frac{\exp(\Delta C_A/RT)\exp(-\Delta H_A/RT)}{\exp(-\Delta H_a'/RT)+\frac{7}{2}F\exp(-\Delta H_c'/RT)}. \tag{25}$$

For self-diffusion $7\omega_c'$ has four basal jumps and three nonbasal jumps and ω_a' and ω_A are equal. If ω_{B0} and ω_{A0} are the jump probabilities of basal and nonbasal jumps for self-diffusion, then

$$f_{A,z:0}=\frac{4.208+2.944(\omega_{B0}/\omega_{A0})}{6.208+2.944(\omega_{B0}/\omega_{A0})}. \tag{26}$$

Mullen[13] has evaluated the ratio ω_{B0}/ω_{A0} using the self-diffusion data for zinc,[6]

$$\omega_{B0}/\omega_{A0}=17\exp(-3.83\times10^3/RT), \tag{27}$$

for$RT=1.1$ kcal/mole, $f_{A,z:0}=0.742$, and $C_{A0}=-0.265$ kcal/mole.

To evaluate C_A we have to evaluate $\Delta H_a'$ and $\Delta H_c'$. These are evaluated as follows.

ΔH_a. In the initial configuration, the vacancy is at a distance λ_A from the impurity. In the saddle-point configuration, the solvent atom will be midway between the initial and final positions, and we assume the two vacancies to be situated at a distance $(11/16)\lambda_A$ on either side of the solvent atom, as shown in Fig. 3:

$$\Delta H_a'=-eV(r_1)-eV(r_2)-\Delta E_A, \tag{28}$$

r_1 and r_2 are the distances of the centroids of the half-vacancies from the impurity. Values of $\Delta H_a'$ are listed in Table II for indium, silver, and gold.

$\Delta H_c'$. In all, there are seven escape jumps. In each of these cases $\Delta H_c'$ has been evaluated by following the procedure outlined for the calculation of $\Delta H_a'$. For positive Z, two of the jumps give negative values and the rest give positive values. The average is calculated as follows:

$$(1/7)\sum\exp(-\Delta H_c'/RT)=\exp[-(\Delta H_c')_{\text{av}}/RT].$$

$(\Delta H_c')_{\text{av}}$ has the same sign as that of Z. For positive Z, the vacancies are attracted by the impurity and the

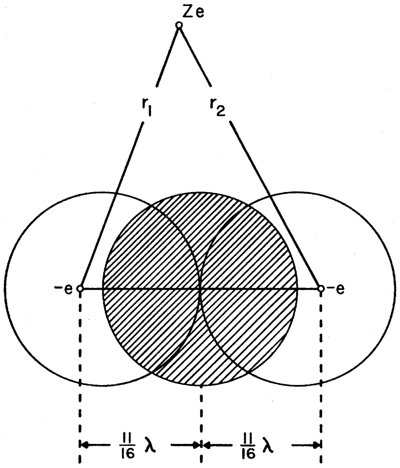

FIG. 3. Saddle-point configuration for a nearest-neighbor solvent jump.

migration of the vacancies away from the impurity atom is made more difficult, and conversely for negative Z values, because of the repulsion between the vacancies and the impurity ion, the escape jumps are made more easier. $(\Delta H_c')_{\mathrm{av}}$ has been evaluated for $RT=1.1$ kcal/mole. This corresponds to $T\approx 280°\mathrm{C}$, which is fairly representative of the midpoints of the temperature ranges of self-diffusion and impurity-diffusion measurements. Values $(\Delta H_c')_{\mathrm{av}}$ are listed in Table II.

We can now use the calculated values of ΔH_A, $\Delta H_a'$, $(\Delta H_c')_{\mathrm{av}}$, $f_{A,z:0}$, and C_0 (see Table II) and the experimental values of $A_{\parallel}$ and $A_{\parallel,0}$ (see Table I) to evaluate C_A. The calculated values of ΔC_A, $f_{A,z}$, and ν_A/ν_{A0} are listed in Table II.

IMPURITY DIFFUSION IN THE PERPENDICULAR DIRECTION

Diffusion of Indium Perpendicular to the *c* Axis

The analysis of the diffusion perpendicular to the c axis is more complicated than the analysis of the parallel diffusion because two types of atomic jumps, basal and nonbasal, are contributing to the perpendicular diffusion. One can express $D_{xx}(=D_{\perp})$ in terms of the lattice parameter a, correlation factors, and energies of formation and motion in the following manner[13]:

$$D_{xx}=D_{\perp}=(a^2/8)f_{B,x}\nu_B\exp(\delta S_B/R)\times\exp[-(H_B+E_B)/RT]+(a^2/24)f_{A,b}\nu_A\times\exp(\delta S_A/R)\exp[-(H_A+E_A)/RT],\quad(29)$$

a is the nearest-neighbor distance in the basal plane; ν_B and ν_A are the corresponding vibrational frequencies; δS, H, and E, with proper subscripts, are the entropy factors, energy of motion, and the energy of formation of a vacancy, respectively; $f_{B,x}$ is the correlation factor for basal jumps; and $f_{A,b}$ is the correlation factor for nonbasal jumps.

TABLE II. Change in the activation energies, correlation factors, etc., for parallel diffusion. (All energies are expressed in units of kcal/mole.)

	Diffusion of indium $Z=+1$	Diffusion of silver $Z=-1$	Diffusion of gold $Z=-1$
α	0.83	1.3	1.3
ΔE_A	-0.655	1.026	1.026
$\Delta H_a'$	0.210	-0.329	-0.329
ΔH_A	-4.933	7.726	7.726
$(\Delta H_C')_{\mathrm{av}}$	0.05	-0.184	-0.184
$A_{\parallel}$	0.062 cm²/sec	0.32 cm²/sec	0.97 cm²/sec
$A_{\parallel,0}$	0.13 cm²/sec	0.13 cm²/sec	0.13 cm²/sec
$fA_{,z:0}$	0.742	0.742	0.742
C_{A0}	-0.265	-0.265	-0.265
ΔC_A	-2.978	0.269	0.266
$(\Delta Q_{\parallel})_{\mathrm{theory}}$	-2.61	8.48	8.48
$(\Delta Q_{\parallel})_{\mathrm{exptl}}$	-2.7	4.2	7.9
$f_{A,z}$	0.363	~ 1	~ 1
ν_A/ν_{A0}	0.065	2.36	6.82

The following expression can be obtained by manipulating the expressions for $D_{\perp}$ and $D_{\parallel}$ [see Eqs. (29) and (4)]:

$$\left[D_{\perp}-\frac{2}{3}\frac{a^2}{c^2}\frac{f_{A,z}}{f_{A,b}}D_{\parallel}\right]\frac{1}{f_{B,x}}=\frac{a^2}{8}\nu_B\exp(\delta S_B/R)\times\exp[-(E_B+H_B)/RT].\quad(30)$$

For zinc,

$$\tfrac{2}{3}a^2/c^2=0.19.$$

Then

$$Y=\Lambda\exp[-(E_B+H_B)/RT],\quad(31)$$

where

$$Y=(1/f_{B,x})[D_{\perp}-0.19(f_{A,z}/f_{A,b})D_{\parallel}]$$

and

$$\Lambda=(a^2/8)\nu_B\exp(\delta S_B/R)=\mathrm{const.}$$

In order to calculate $f_{B,x}$ and $f_{A,b}$, it is necessary to solve the following simultaneous equations for $S_{B,x}$ and $S_{A,b}$:

$$S_{B,x}\left[2+\frac{\omega_b}{\omega_a}+7F\frac{\omega_c}{\omega_a}+2\frac{\omega_B}{\omega_a}\right]=\sqrt{3}S_{A,b}-\frac{\omega_B}{\omega_a}\lambda_B,\quad(32)$$

$$S_{A,b}\left[2+3\frac{\omega_b'}{\omega_a'}+7F\frac{\omega_c'}{\omega_a'}+2\frac{\omega_A}{\omega_a'}-\left(2+3\frac{\omega_b}{\omega_a}+7F\frac{\omega_c}{\omega_a}+\frac{\omega_B}{\omega_a}\right)^{-1}\right]=\sqrt{3}S_{B,x}-\left(\frac{\omega_A}{\omega_a'}\right)\lambda_{A,b}.\quad(33)$$

These simultaneous equations are obtained by manipulating Eqs. (14), (15), and (16). To solve Eqs. (32) and (33), ω_b/ω_a, ω_c/ω_a', etc. have been evaluated at three temperatures corresponding to $RT=0.9$, 1.1, and 1.3 kcal/mole.

Typically,

$$\frac{\omega_B}{\omega_a}=\frac{\omega_B}{\omega_{B0}}\frac{\omega_{B0}}{\omega_{A0}}\frac{\omega_{A0}}{\omega_a},$$

$$\omega_B/\omega_{B0}=(\nu_B/\nu_{B0})\exp(-\Delta H_B/RT),$$

$$\omega_{B0}/\omega_{A0}=17\exp[-(3.83\times10^3)/RT],^{13}$$

and

$$\omega_a/\omega_{A0}=(\nu_a/\nu_{A0})\exp(-\Delta H_a/RT).$$

We note that ν_B and ν_{B0} correspond to the atomic frequencies of the impurity and solvent ions. We will assume that

$$\nu_B/\nu_{B0}=\nu_A/\nu_{A0}=0.065$$

(see Table II).

Since ν_a and ν_{A0} correspond to the atomic frequencies of zinc atoms, following Manning,[16] we set $\nu_a/\nu_{A0}=1$.

TABLE III. Changes in the activation energies required to calculate $f_{A,b}$ and $f_{B,x}$ for the diffusion of indium tracer: $Z=+1$; $\alpha=0.83$. (All energies expressed in units of kcal/mole.)

ΔE_B	ΔH_B	ΔH_a	ΔH_b	ΔH_c	$\Delta H_a'$	$\Delta H_b'$	$\Delta H_c'$
−1.166	−7.387	0.722	0.556	0.103	0.210	0.291	0.050

It is possible to calculate ΔH_B and ΔH_a by considering the disposition of the moving atom and the vacancy in the equilibrium and saddle-point configurations with reference to the impurity. Table III summarizes the values of ΔH_a, ΔH_b, $\Delta H_b'$, etc. The simultaneous equations are then solved for $S_{A,b}$ and $S_{B,x}$, and these in turn are substituted in Eqs. (17) and (18) to obtain the values of $f_{A,b}$ and $f_{B,x}$ at three different temperatures. Table IV summarizes the values of the correlation factors. Table V summarizes the values of Y [that have been calculated by using the experimental values[4] of $D_{\parallel}$ and $D_{\perp}$ (see Table I)] at these three temperatures and the estimated values of the correlation factors. Figure 4 shows a plot of Y versus $1000/T$ on a semilog scale. These three points lie fairly well on a straight line. From the slope of this straight line, E_B+H_B has been determined and this turns out to be 15.98 kcal/mole.

TABLE IV. Correlation factors pertaining to the diffusion of indium tracer.

$RT\times10^{-3}$	t (°C)	$f_{A,z}$	$f_{A,b}$	$f_{B,x}$
0.9	180	0.171	0.124	0.045
1.1	280.7	0.363	0.287	0.095
1.3	381	0.535	0.455	0.156

TABLE V. Diffusion coefficients $D_{\parallel}$ and $D_{\perp}$, and Y (in units of cm²/sec) as a function of temperature for indium tracer.

$RT\times10^{-3}$	$D_{\parallel}$	$D_{\perp}$	Y
0.9	3.764×10^{-11}	4.878×10^{-11}	9.687×10^{-10}
1.1	1.784×10^{-9}	2.558×10^{-9}	2.411×10^{-8}
1.3	2.580×10^{-8}	3.966×10^{-8}	2.275×10^{-7}

A similar analysis has been carried out to evaluate $E_{B0}+H_{B0}$ for self-diffusion[6] (see Table I). We note that

$$7\omega_c=4\omega_{A0}+3\omega_{B0}:7\omega_c'=3\omega_{A0}+4\omega_{B0},$$

$$\omega_A=\omega_a'=\omega_a=\omega_{A0}:\omega_B=\omega_b'=\omega_b=\omega_{B0}.$$

We have evaluated $f_{A,z}$, $f_{A,b}$, and $f_{B,x}$ at two temperatures, corresponding to $(1000/T)=2$ and 1.5. This choice of the temperatures was made because Mullen[13] has used the experimental values of $D_{\perp}/D_{\parallel}$ at these two temperatures to evaluate ω_{B0}/ω_{A0} from his analysis. Table VI shows the correlation factors at these two temperatures. The bracketed values in the table are the correlation factors interpolated from the table of correlation factors given by Mullen.[13] As Table VI shows, the correlation factors evaluated by using Eqs. (13), (17), and (18) check fairly well with the values obtained by Mullen[13] using a different technique. After the analysis is carried through, we obtain

$$E_{A0}+H_{A0}=21.53 \text{ kcal/mole},$$

$$E_{B0}+H_{B0}=26.16 \text{ kcal/mole},$$

$$(E_B+H_B)-(E_{B0}+H_{B0})=15.98-26.16$$
$$=-10.18 \text{ kcal/mole}.$$

From Table II we have $\Delta E_B+\Delta H_B=-8.55$ kcal/mole.

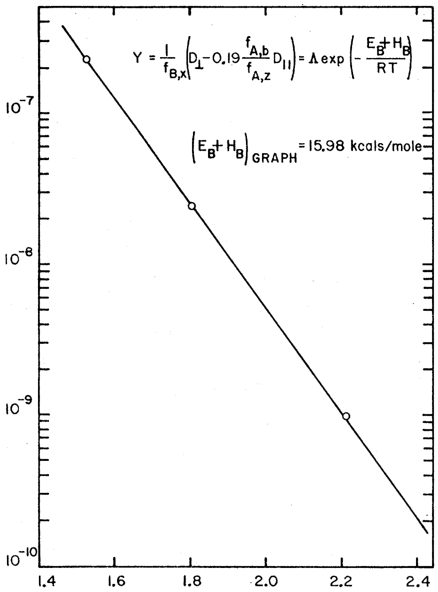

FIG. 4. A plot of Y versus $1000/T$ to determine E_B+H_B.

TABLE VI. Correlation factors pertaining to self-diffusion.

$1000/T$	ω_{B0}/ω_{A0}	$f_{A,z}$	$f_{A,b}$	$f_{B,x}$
2.0	0.360	0.725) (0.716)	0.702 (0.716)	0.851 (0.849)
1.5	0.944	0.777 (0.776)	0.775 (0.778)	0.784 (0.788)

Diffusion of Silver and Gold Perpendicular to the *c* Axis

We shall assume that $\nu_A=\nu_B=\nu$ and $\delta S_A=\delta S_B=\delta S$ [see Eq. (29)] and substitute the estimated values of ΔE_B, ΔH_B, ΔE_A, and ΔH_A (for $Z=-1$) to calculate E_B+H_B and E_A+H_A. One can then express $D_{\perp}$ in the following manner:

$$D_{\perp}=(a^2/24)\exp(\delta S/R)\exp(-30.29\times10^3/RT)$$
$$\times[1+3\exp(-9.27\times10^3/RT)].$$

The bracketed quantity is evaluated at three temperatures corresponding to $RT=0.9$, 1.1, and 1.3 kcal/mole:

RT	$[1+3\exp(-9.27\times10^3/RT)]$
0.9×10^3	~1.0002
1.1×10^3	~1.0006
1.3×10^3	~1.0024

The bracketed quantity differs from 1 only by a fraction of a percent. This indicates that the contribution of the nonbasal jumps to the perpendicular diffusion is predominant and that the activation energy for the perpendicular diffusion will be almost equal to that for the parallel diffusion. Therefore

$$(Q_\perp)_{\text{theory}}\sim(Q_{\parallel})_{\text{theory}}=E_A+H_A=30.29\text{ kcal/mole};$$

for silver[4]:

$$(Q_{\parallel})_{\text{exptl}}=26.0\text{ kcal/mole},$$
$$(Q_\perp)_{\text{exptl}}=27.6\text{ kcal/mole};$$

for gold[5]:

$$(Q_{\parallel})_{\text{exptl}}=29.7\text{ kcal/mole},$$
$$(Q_\perp)_{\text{exptl}}=29.7\text{ kcal/mole}.$$

DISCUSSION

We have assumed that a solute atom differs from atoms of solvent only in its possession of a different ionic charge, and that the difference Ze is concentrated as a point charge at the center of the solute atom. We have calculated the potential around the impurity in the Thomas–Fermi approximation. The inner cores of the solutes (In, Ag, and Au)[4,5] studied so far are different from that of the zinc atom. The effect of the core of the solute (different from that of the solvent atom) in primary solid solutions has been studied by Friedel.[20] This effect leads to a polarization of the electron density in the neighborhood of the solute. This would contribute further to the screening charge cloud and would affect the potential around the solute. We have neglected this effect. Recent calculations of Kohn and Vosko,[21] of Langer and Vosko,[22] and of others indicate that the potential around an impurity in cubic metals shows an oscillatory behavior instead of falling monotonically. They have shown that the curvature of the potential at the nearest-neighbor distance is different from the one obtained by using Thomas–Fermi potential. Probably the potentials around an impurity and a vacancy in zinc also have such an oscillatory behavior. The potentials may not be spherically symmetric in the zinc matrix. A precise calculation of the potential around an isolated impurity or an isolated vacancy is complex. The magnitude of the complexity is increased when the impurity and vacancy are adjacent to each other, because of the local charge redistribution and relaxation of the lattice. Certainly the local charge redistribution and its interaction with the impurity in the saddle-point configuration cannot be calculated without drastic assumptions. Correlation effects would certainly add their share of complexity to the problem of evaluating the activation energy for diffusion. In the absence of any detailed calculations for the potentials of the impurity and vacancy (even the isolated ones) in zinc, it is as good a starting point as any to use a Thomas–Fermi approximation in an attempt to understand impurity diffusion in a divalent metal zinc, exploiting the information available on the impurity diffusion in monovalent metals.

Diffusion of Indium

From Table II, we note that, for parallel diffusion,

$$(\Delta Q_{\parallel})_{\text{theory}}=(\Delta H_A+\Delta E_A)-\Delta C_A$$
$$=-5.59+2.98=-2.61\text{ kcal/mole}$$

and

$$(\Delta Q_{\parallel})_{\text{exptl}}=-2.7\text{ kcal/mole}.$$

$(\Delta Q_{\parallel})_{\text{theory}}$ checks with the experimental value within 4%. The calculations show that correlation correction is of considerable importance. We note that the correlation factor $f_{A,z}(0.363)$ for diffusion of indium tracer is smaller than $f_{A,z:0}(0.743)$, and that is what we expect. This is consistent with the concept that the diffusion jumps are highly correlated because of the strong attraction between the impurity and a vacancy.

The ratio of the vibrational frequencies ν_A/ν_{A0} is less than 1 ($\nu_A/\nu_{A0}=0.065$). LeClaire[3] has shown that ν_A/ν_{A0} should be fractional for Z positive and greater than 1 for Z negative. This does not contradict the experimental fact that indium diffuses faster than zinc. The relative diffusion rates are determined by the ratios ω_A/ω_{A0} and ω_B/ω_{B0}. For example,

$$\omega_A/\omega_{A0}=(\nu_A/\nu_{A0})\exp(-\Delta H_A/RT)$$
$$=5.8\text{ for }RT=1.1\times10^3\text{ cal/mole}.$$

Similarly it can be shown that $\omega_B/\omega_{B0}>1$.

The analysis of the diffusion perpendicular to the c axis is rather involved because of the two types of diffusion jumps. Before one can estimate the activation energy (E_B+H_B) for basal jumps from the data of perpendicular and parallel diffusion, the knowledge of the magnitudes of the correlation factors and also their temperature variation is necessary. The correlation factors evaluated at three different temperatures are listed in Table IV. In the calculation we have made use of the ratio ν_A/ν_{A0}, obtained from the analysis of the parallel diffusion. Another reasonable assumption has been made, namely, $\nu_A/\nu_{A0}=\nu_B/\nu_{B0}$. It is interesting to note that $f_{B,x}$ is very small and strongly supports the viewpoint that motion of the indium in the basal plane

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is highly correlated as a result of the strong attraction between the indium and a vacancy. In fact the position of a vacancy in the same basal plane as that of the indium atom and at an adjoining site is energetically a favorable configuration. The small value of $f_{B,x}$ may be interpreted as suggesting that indium–vacancy pairs stay together for a considerable length of time. Table IV shows that correlation factors increase with the increase in temperature. This is reasonable because the motions of the atoms become more random with increase in temperature and hence less correlated.

The activation energy for basal diffusion (only basal jumps involved) is determined by using the experimental data and the calculated values of the correlation factors, and this turns out to be 15.98 kcal/mole. We have determined $E_{B0}+H_{B0}$ by making use of the self-diffusion data and the calculated correlation factors. This turns out to be 26.16 kcal/mole.

$$\begin{aligned}(\Delta Q_{\text{basal}})_{\text{exptl}} &= E_B+H_B-(E_{B0}+H_{B0})\\ &=15.98-26.16\\ &=-10.18 \text{ kcal/mole},\end{aligned}$$

$$(\Delta Q_{\text{basal}})_{\text{theory}}=\Delta E_B+\Delta H_B=-8.55 \text{ kcal/mole}.$$

The theoretical and experimental values differ by 16%. This difference is felt to be not too serious because the evaluation of $(\Delta Q_{\text{basal}})_{\text{exptl}}$ involves the numerical estimates of the correlation factors which in turn depend on the ratios of the jump rates such as ω_A/ω_a', etc. These ratios are calculated using the estimates of ΔH_A, ΔH_B, $\Delta H_a'$, etc. The ratio ν_A/ν_{A0} determined from the analysis of the parallel diffusion has been used to determine some of the ratios of the jump rates. It may be noted that evaluation of ν_A/ν_{A0} involves the use of experimental values of the frequency factors $A_{\parallel}$ and $A_{\parallel,0}$. With all these considerations taken into account, it may be said that the theoretical estimate checks fairly well with the experimental value.

Diffusion of Silver and Gold

As Table I shows, the correlation factors for parallel diffusion in the two cases are almost equal to unity and suggest that the diffusion jumps are uncorrelated. The correlation correction ΔC_A is negligible.

The experimental values of $(\Delta Q_{\parallel})$ are as follows:

$$\begin{aligned}(\Delta Q_{\parallel})_{\text{exptl}} &= 4.2 \text{ kcal/mole for silver}^4\\ &=7.9 \text{ kcal/mole for gold.}^5\end{aligned}$$

Our calculations predict the same change in activation energies for both these impurities, since each has an excess charge $Z=-1$:

$$(\Delta Q_{\parallel})_{\text{theory}}=8.48 \text{ kcal/mole}.$$

The predicted value of $(\Delta Q_{\parallel})_{\text{theory}}$ checks with $(\Delta Q_{\parallel})_{\text{exptl}}$ for gold within 7%, whereas $(\Delta Q_{\parallel})_{\text{exptl}}$ for silver is nearly 50% smaller than the predicted value. This discrepancy suggests that the effective excess charge Z of silver is possibly greater than -1 (and less than zero).

Our calculations of $\Delta E_B+\Delta H_B$ and hence E_B+H_B suggest that a major contribution to the perpendicular diffusion comes from the nonbasal jumps. If the perpendicular diffusion were to take place entirely due to nonbasal jumps, then one would expect the anisotropy $(D_{\parallel}/D_{\perp})$ to be ≈ 5.2 for zinc. However, $D_{\parallel}/D_{\perp}$ is approximately 3.3 in the case of gold diffusion, and of the order of 2 in the case of silver diffusion. This suggests that both types of jumps are probably contributing to the perpendicular diffusion.

One may note that silver diffuses faster than gold, even in gold–silver solid solutions, throughout the whole range of composition.[23] A more precise analysis would require a better potential around an impurity, which would include the effects of the core of the impurity atom.

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