Impurity Diffusion in Cadmium†

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Diffusion of impurities in single crystals of cadmium has been studied by tracer-sectioning techniques. For heterovalent diffusion the diffusion coefficients, in cm^2/sec, are given by $D_\parallel(In) = \exp(-2.29 \pm 0.20) \exp[-(17.45 \pm 0.19)1000/RT]$, $D_\perp(In) = \exp(-2.41 \pm 0.16) \exp[-(16.94 \pm 0.15)1000/RT]$, $D_\parallel(Ag) = \exp(0.34 \pm 0.47) \exp[-(24.64 \pm 0.48)1000/RT]$, $D_\perp(Ag) = \exp(-0.39 \pm 0.62) \exp[-(25.07 \pm 0.65)1000/RT]$, $D_\parallel(Au) = \exp(0.34 \pm 0.08) \exp[-(25.47 \pm 0.08)1000/RT]$, and $D_\perp(Au) = \exp(1.15 \pm 0.22) \exp[-(26.43 \pm 0.22)1000/RT]$. The activation energies obtained in this study could be interpreted with LeClaire's screening model. Good agreement between experimental results and theoretical estimates was obtained. For homovalent diffusion (including self-diffusion), the results are $D_\parallel(Zn) = \exp(-2.04 \pm 0.26) \exp[-(18.03 \pm 0.25)1000/RT]$, D (Zn) $= \exp(-2.48 \pm 0.24) \exp[-(18.02 \pm 0.24)1000/RT]$, $D_\parallel(Cd) = \exp(-2.14 \pm 0.13) \exp[-(18.61 \pm 0.12)1000/RT]$, $D_\perp(Cd) = \exp(-1.70 \pm 0.19) \exp[-(19.59 \pm 0.19)1000/RT]$, $D_\parallel(Hg) = \exp(-1.55 \pm 0.07) \exp[-(18.78 \pm 0.06)1000/RT]$, and $D_\perp(Hg) = D_\parallel(Hg)$. It is felt that valence and size effects are in competition for homovalent diffusion. The size effect appears dominant in the case of Cd as the base metal, whereas for Zn as the base metal the valence effect seems to dominate. A preliminary study of the isotope effect of Zn in Cd was also conducted. The resulting values of E for diffusion parallel and perpendicular to the c axis were 0.4388 ± 0.0495 and 0.6829 ± 0.1023 at 199.3 °C. These results seems to rule out the interstitial mechanism as the dominant mechanism in agreement with the usual assumption that the vacancy mechanisms (basal and nonbasal) prevail for the hexagonal metals.

I. INTRODUCTION

Recently considerable interest has been shown in measuring diffusivities in noncubic metals, where the diffusion is anisotropic. Self-diffusion data exist for Zn,[1,2] Cd,[3-5] Mg,[6] In,[7] Tl,[8] Sb,[9,10] and Bi.[11] The largest body of impurity diffusion work has been done with zinc using the standard sectioning technique. Accurate data for both directions, parallel and perpendicular to the c axis, have been reported for the following solutes: Cu,[12] Ga,[12] Ag,[13] In,[13] Au,[14] Cd,[14] Hg,[15] and Sn.[16] The general trend of the activation energy with the valence of the diffusing element lends support to the assumption that the diffusion is taking place via basal and nonbasal vacancy mechanisms. The observed reversal of anisotropy between the diffusion for monovalent and trivalent impurities is explained in terms of a shielded electrostatic interaction between the impurity ion and the vacancy.

Ghate,[17] after the correlation factor for the hcp structure had been developed, applied LeClaire's theory of heterovalent diffusion to impurities In, Ag, and Au diffusing in Zn. The results compare fairly well with the experimentally measured values in the cases of In and Au, but a considerable discrepancy exists for Ag. Subsequently, Batra applied Ghate's values to the impurities Cu[12] and Ga[12] diffusing in Zn, and obtained good agreement for Cu but poor agreement for Ga. A similar attempt[15] to apply LeClaire's theory of homovalent diffusion to the impurities Cd and Hg diffusing in

Zn has also been performed. While a qualitative explanation for the Cd case was obtained, it appears that the size effect, in the Hg case, might play an important role. Double-isotope studies of the diffusion of Zn[2,18] and Cd[18] in Zn firmly established the vacancy (basal and nonbasal) mechanisms as responsible for diffusion in the Zn matrix. It was found that an attractive interaction exists between the cadmium impurity and the vacancy, the interaction being larger when both are in the same basal plane.

With the idea of checking to what extent LeClaire's models would apply to diffusion in cadmium, the author decided to study the diffusion of the impurities Zn, Hg, Ag, In, and Au in Cd. To check the anisotropy in the diffusion constants, the self-diffusion experiment was repeated. A study of the impurity isotope effect using Zn^{65} and Zn^{69m} was also undertaken in order to check whether the interstitial mechanism could be operative in this case.

II. EXPERIMENTAL TECHNIQUE

Single crystals were grown by the Bridgman method from 99.999%-pure cadmium supplied by Cominco. Only those crystals which had their cylindrical axes closely parallel or perpendicular to the hexagonal axis were retained for the experimental work. Diffusion samples $\frac{1}{2}$ in. in diameter and $\frac{3}{8}$ in. long were cut by a specially designed multiple-string saw. The preparation procedures of these specimens were similar to that outlined by

TABLE I. Plating baths for impurities.

Isotope	Source	Plating bath	
Zn^{65} (2 mCi)	New England Nuclear Corp., Boston, Mass.	H_2O NaCN NaOH Zn^{65} Temperature 50 °C	100 cm^3 2.3 g 5.3 g in HCl solution
Ag^{110} (1 mCi)	New England Nuclear Corp., Boston, Mass.	H_2O KCN K_2CO_3 Ag^{110}	100 cm^3 6.0 g 4.5 g in HNO$_3$ solution
Cd^{109} (2 mCi)	New England Nuclear Corp., Boston, Mass.	H_2O NaCN NaOH Cd^{109}	100 cm^3 2.3 g 5.3 g in HCl solution
Au^{195} (1 mCi)	New England Nuclear Corp., Boston, Mass.	H_2O KOH KCN Au^{195}	0.7 cm^3 0.3 cm^3 0.65 gm^3 in HCl solution
Hg^{203} (2 mCi)	New England Nuclear Corp., Boston, Mass.	Hg^{203}	in HNO$_3$ solution
In^{114m} (3 mCi)	Union Carbide Corp. P.O. Box 324, Tuxedo, N. Y. 10984	In^{114m} in HCl solution; double plating in InCl$_3$ and H_2O solution	
Zn^{69m} (12 mCi) and Zn^{65} (4 mCi)	Union Carbide Corp., P.O. Box 324, Tuxedo, N. Y. 10984	Same as Zn^{65} bath	

Rosolowski[13] for zinc.

The plating baths for deposition of various impurities are shown in Table I. A current density of about 20 mA/cm^2 was used during electroplating. Chemical platings were used for Ag, Au, Hg, and In, where no external voltage was applied.

For each diffusion anneal, two samples, one parallel and one perpendicular, were vacuum sealed in a Pyrex capsule evacuated to better than 10^{-6} Torr. Their active faces were separated by a thin Pyrex disk to minimize the evaporation of the plated material. A glass slug was put in to reduce the empty space available to impurity vapor. The diffusion anneals lasted from 1 h to 2 mos. The temperatures were controlled within ± 0.5 °C over these periods. They were measured by chromel-alumel thermocouples connected to a Leeds and Northrup Type K-4 precision potentiometer and recorded by a Leeds and Northrup multipoint recorder. After each run, the monitoring thermocouple was calibrated against a standard NBS Pt–Pt-10%-Rh thermocouple. The initial warmup time correction, typically 3 min, was calculated and applied. The capsule was quenched in ice water after each run. After the diffusion anneal, the samples were analyzed by the standard sectioning technique.

For the preliminary isotope effect of zinc diffu-

sion in cadmium, the total γ radiation above a lower-level discriminator was counted to 10^5 impulses or more for six times over a period of about 3 days. The ratio of the activities of Zn^{69m} and Zn^{65} was obtained by a least-squares fitting of these data. Corrections were made for dead time, background, and counter drift.

III. RESULTS

The penetration profiles shown in Fig. 1 for zinc are typical. The Arrhenius plots are shown in Figs. 2–7. The parameters derived from a least-squares fit to these data are given in Table II. The isotope-effect data are given in Table III. Figure 8 shows the computer-fitted plots of $\ln(C_{65}/C_{69})$ vs $\ln C_{65}$ for diffusion of zinc in two cadmium single crystals at 199.3 °C.

IV. THEORY AND APPLICATIONS

The electrostatic-interaction theory proposed by Lazarus[19] and later modified by LeClaire[20, 21] has proven successful in explaining the over-all pattern for impurity diffusion in the fcc noble metals and hcp zinc. In this model, the vacancy mechanism is assumed and the screened Coulombic interaction between a vacancy and an impurity atom is considered to be dominant.
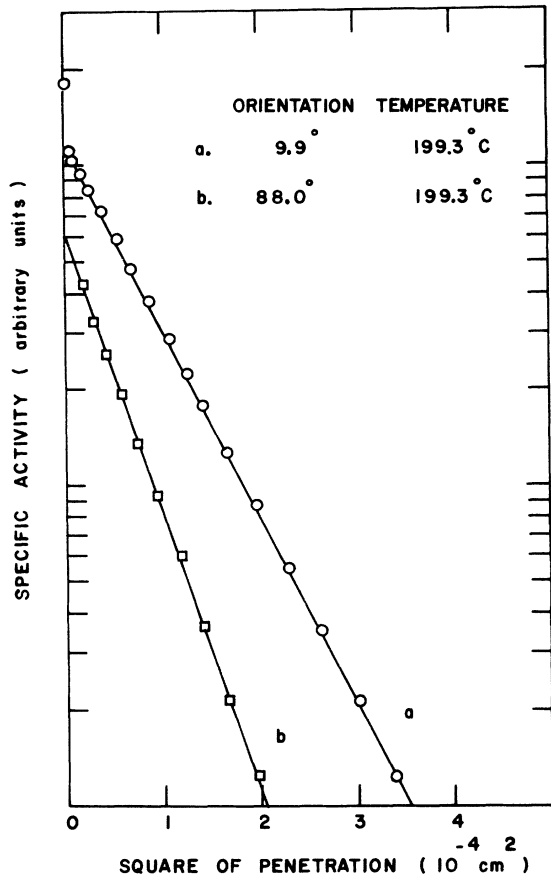
FIG. 1. Penetration profiles for diffusion of Zn in Cd.

A. Le Claire's Heterovalent Theory for Diffusion of In, Ag, and Au in Cu

The change in activation energy for impurity diffusion can be expressed by the relation

$$\Delta Q = \Delta E_f + \Delta H_2 - \Delta C , \qquad (1)$$

where ΔE_f is the difference between the energy to form a vacancy next to an impurity atom and the energy to form a vacancy in the pure solvent. ΔH_2 is the difference between the energy for a vacancy-impurity atom exchange and the energy for a vacancy-solvent atom exchange in the pure solvent. The ΔC term arises form the difference between the temperature dependence of the correlation factor for impurity diffusion and that for self-diffusion. The existence of a temperature dependence in the correlation factor for self-diffusion is due to the fact that there is more than one kind of vacancy jump frequency governing diffusion in anisotropic crystals. The expression for C is

$$C = R \frac{\partial \ln f}{\partial (1/T)} , \qquad (2)$$

where f is the corresponding correlation factor.

Evaluations of ΔE_f, ΔH_2, and ΔC are obtained from the electrostatic potential of the charge of $-Z$ (solvent) e on a vacancy and the potential $V(r)$ arising from the screened point charge [$Z = Z$(solute) $- Z$(solvent)]. The expressions for ΔE_f and ΔH_2 are (in a divalent solvent)

$$\Delta E_f = - 2eV(\lambda) \qquad (3)$$

and

$$\Delta H_2 = - 2eV(\tfrac{11}{16}\lambda) - \Delta E_f , \qquad (4)$$

where λ is the jump distance. $\tfrac{11}{16} \lambda$ is the distance between the impurity and the centroids of the half-vacancy hemispheres that flank the impurity at the saddle point. Atom relaxation displacements are neglected.

The potential $V(r)$ around the impurity ion is calculated from the Thomas-Fermi screening potential, as given by the expressions

$$V(r) = \alpha(Ze/r) e^{-qr}$$

and $\qquad (5)$

$$q^2 = (4me^2/\hbar^2)(3n_0/\pi)^{1/3} ,$$

where q is the screening parameter characterizing the solvent, α is a constant depending on Z with a value around unity, and n_0 is the number of electrons per unit volume. For cadmium the lattice parameters $a = 2.9787$ Å and $c = 5.617$ Å were used to give the results $n_0 = 9.2677 \times 10^{22}/\text{cm}^3$ and $q = 1.836 \times 10^8/\text{cm}$. The Fermi energy of Cd electrons is given by

$$E_m = (\hbar^2/2m)(3n_0/\pi)^{2/3} = 1.20 \times 10^{-11} \text{ erg}.$$

The constant α was determined by using the master solution given by Umeda and Koboyashi[22] for $Z = + 1$, and by using the method developed by Alfred and March[23, 24] for $Z = - 1$.

TABLE II. Parameters for impurity and self-diffusion in Cd.

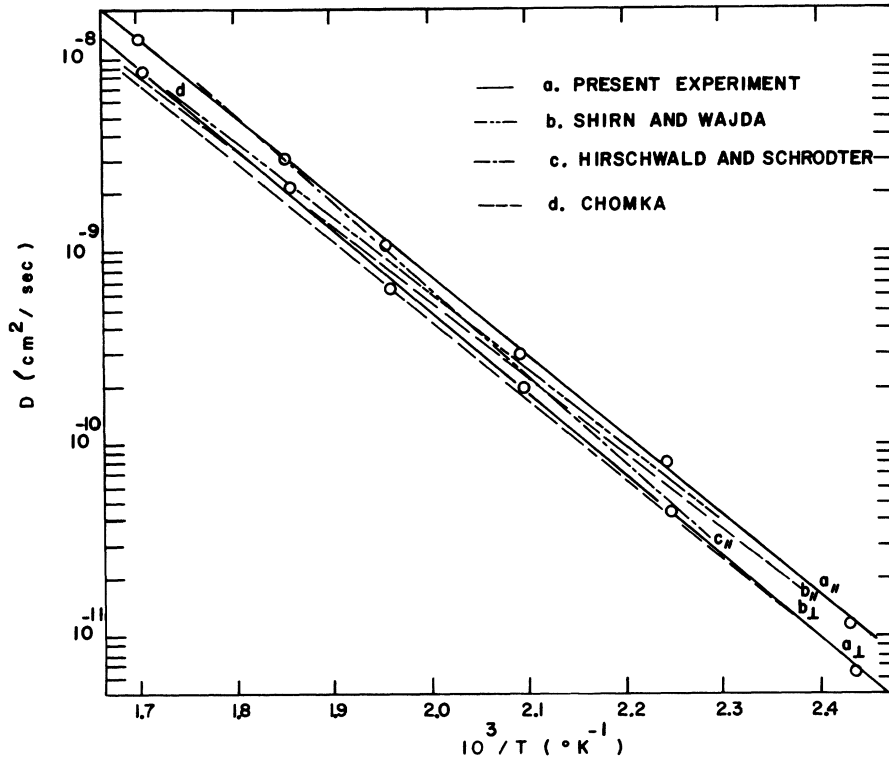| Tracer	Orientation (deg)	$\ln D_0$ (cm²/sec)	Q (kcal/mole)
Cd	0	-2.14 ± 0.13	18.61 ± 0.12
	90	-1.70 ± 0.19	19.59 ± 0.19
Zn	0	-2.04 ± 0.26	18.03 ± 0.25
	90	-2.48 ± 0.24	18.02 ± 0.24
Ag	0	$+0.34 \pm 0.47$	24.64 ± 0.48
	90	-0.39 ± 0.62	25.07 ± 0.65
In	0	-2.29 ± 0.20	17.45 ± 0.19
	90	-2.41 ± 0.16	16.94 ± 0.15
Hg	0 and 90	-1.55 ± 0.07	18.78 ± 0.06
Au	0	$+0.34 \pm 0.08$	25.47 ± 0.08
	90	$+1.15 \pm 0.22$	26.43 ± 0.22

FIG. 2. Temperature dependence of D for self-diffusion in Cd.

The calculated results for various energies for A jump (nonbasal jump) and B jump (basal jump) are listed in Table IV.

The calculation of C requires the knowledge of the correlation factors. The expression for the correlation factors in anisotropic material has been developed by Huntington and Ghate.[25] Some errors were found in the equation in the example of the method for the case for impurity diffusion in the hcp lattice shown in the original papers.[25,17] Using the same notation as illustrated by Fig. 9, we give the corrected equations as follows:

$$S_{A,z} = \frac{2w_b' S_{A,z} - w_A(\lambda_{A,z} + S_{A,z})}{2w_a' + 2w_b' + 7Fw_c' + w_A} , \qquad (6)$$

$$S_{A,b} = \frac{\sqrt{3}w_a^{\frac{1}{2}} S_{B,x} + 2w_b'(-\frac{1}{2})S_{A,b} - w_A(\lambda_{A,b} + S_{A,b})}{2w_a' + 2w_b' + 7Fw_c' + w_A} , \qquad (7)$$

$$S_{B,x} = \frac{\sqrt{3}w_a S_{A,b} + 2w_b(\frac{1}{2})S_{B,x} - w_B(\lambda_B + S_{B,x})}{2w_a + 2w_b + 7Fw_c + w_B} , \qquad (8)$$

TABLE III. Isotope effect for Zn^{65} and Zn^{69m} in Cd.

Sample	Temp.	Orientation (deg)	$D^{65}/D^{69} - 1$	E^{65}_{69m}
a	199.3	9.9	0.0133 ± 0.0015	0.438 ± 0.049
b	199.3	88.0	0.0207 ± 0.0031	0.683 ± 0.102

where the vectors $\vec{S}$ are closely antiparallel to the last jump that the impurity atom made and repre-

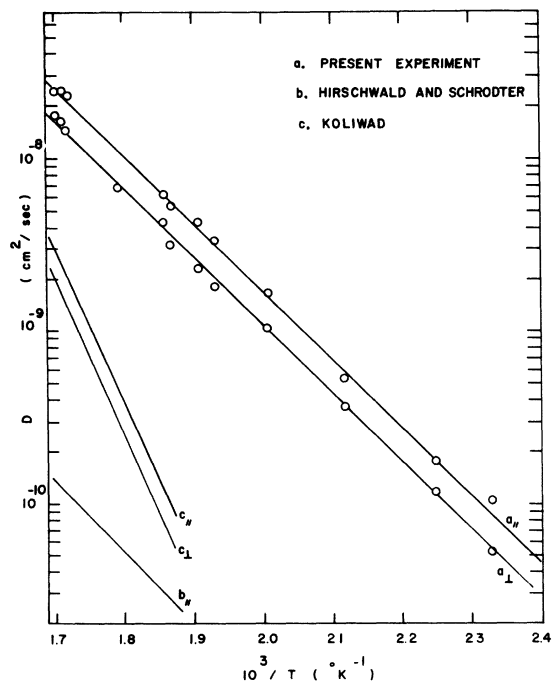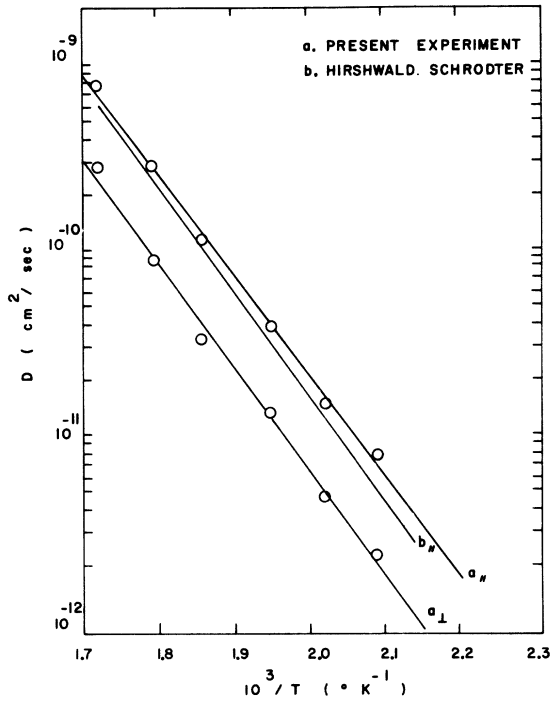FIG. 3. Temperature dependence of D for diffusion of Zn in Cd.

FIG. 4. Temperature dependence of D for diffusion of Ag in Cd.

FIG. 6. Temperature dependence of D for diffusion of Hg in Cd.

sent the expectation value of the vector sum of the subsequent jumps for the impurity in that configuration. After using the 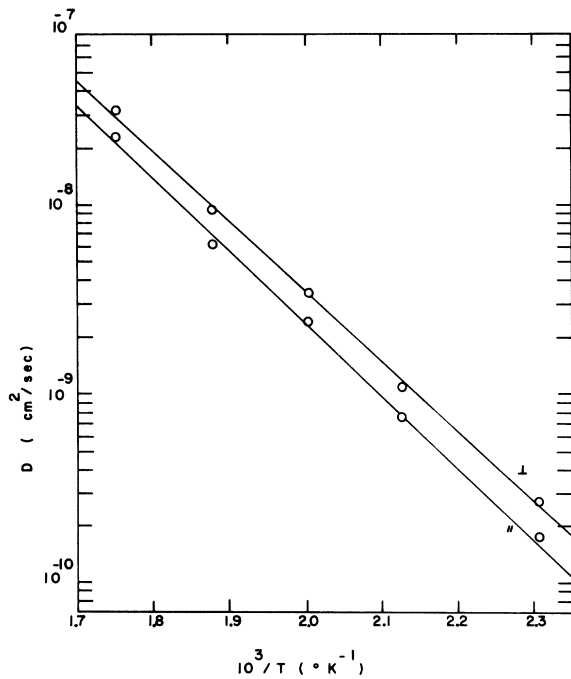relations $\lambda_{A,z} = \frac{1}{2}c$, $\lambda_{A,b}$ $= \frac{1}{3}a$, and $\lambda_B = a$, the correlation factors have the following expressions:

$$f_{A,z} = \frac{2w_a' + 7Fw_c'}{2w_a' + 2w_A + 7Fw_c'} \quad , \tag{9}$$

FIG. 5. Temperature dependence of D for diffusion of In in Cd.
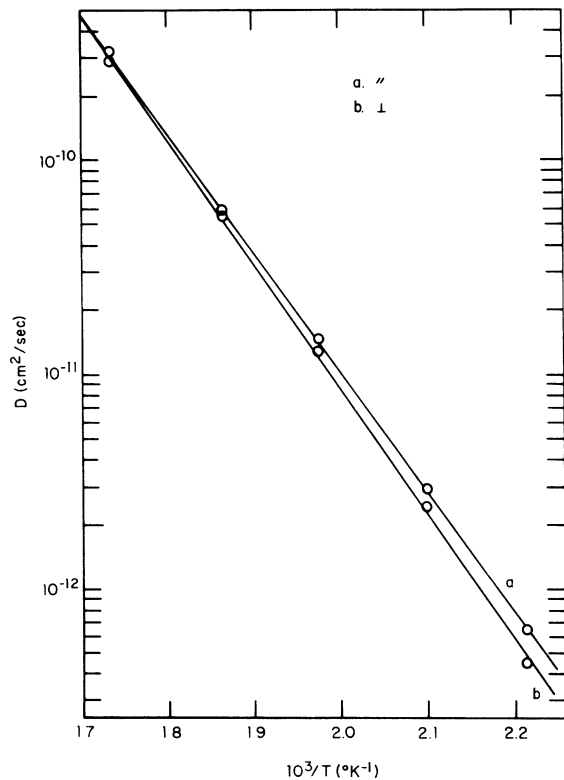

FIG. 7. Temperature dependence of D for diffusion of Au in Cd.

TABLE IV. Changes in the activation energies. (All values are in units of kcal/mole.)

	$Z = +1$	$Z = -1$
α	0.772	1.36
ΔE_A	-0.367	0.647
ΔH_A	-3.166	5.576
$\Delta H'_a$	0.108	-0.191
$\Delta H'_b$	0.168	-0.296
$\Delta H'_{c_{av}}$	0.019	-0.088
ΔE_B	-0.724	1.275
ΔH_B	-5.083	8.955
ΔH_a	0.465	-0.819
ΔH_b	0.358	-0.630
$\Delta H_{c_{av}}$	0.067	-0.303

$$f_{A,b} + \left(\frac{-2 - w_b}{w_a} - \frac{7Fw_c}{w_a} - \frac{2w_B}{w_a} \right) f_{B,x}$$

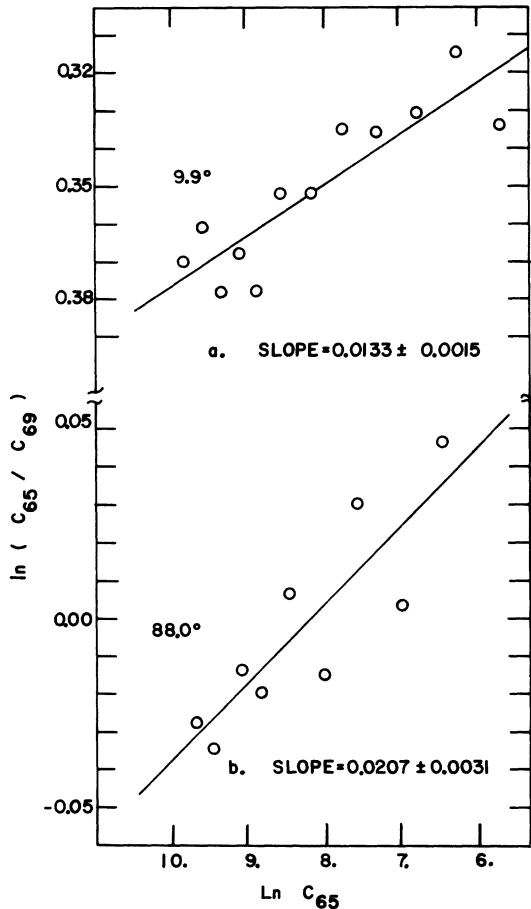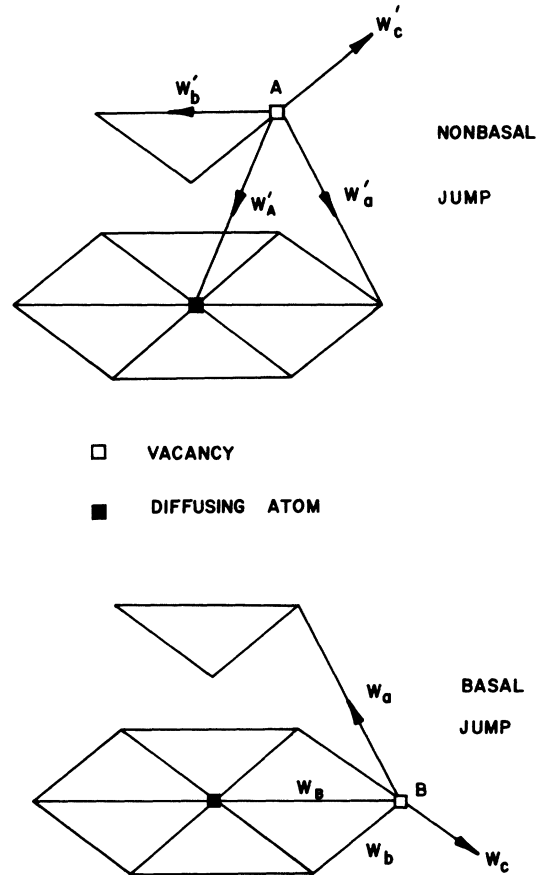$$= -1 - \frac{w_b}{w_a} - \frac{7Fw_c}{w_a} \ , \quad (10)$$

FIG. 9. Configurations for vacancy mechanisms in hcp crystals.

FIG. 8. $\ln(C_{65}/C_{69})$-vs-C_{65} plot for diffusion of Zn isotopes in Cd.

$$\left(2 + \frac{3w'_b}{w'_a} + \frac{7fw'_c}{w'_a} + \frac{2w_A}{w_a} \right) f_{A,b} - 3f_{B,x}$$

$$= -1 + \frac{3\,w'_b}{w'_a} + \frac{7Fw'_c}{w'_a} \ . \quad (11)$$

A comparison of these relations with the original paper[17] will show that the error in that paper is the introduction of an extra term, $S_{B,y}$, in the equations. However, the effect of this error is too small to cause any significant change in the final results.

1. Impurity Diffusion in Parallel Direction

Assuming an exponential temperature dependence for the frequency factors as predicted by reaction-rate theory, a table given by Mullen,[26] and using our experimental results for Cd self-diffusion, we obtain the ratio of basal to nonbasal jump frequencies as

$$w_{B0}/w_{A0} = 4.76 \exp(-2.041 \times 10^3/RT) \ . \quad (12)$$

From Eqs. (9) and (12), taking the vacancy escape

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

$1000/RT$	$f_{A,z}$	$f_{A,b}$	$f_{B,x}$
0.90	0.455	0.332	0.127
1.05	0.273	0.206	0.074
1.20	0.176	0.120	0.059

efficiency $F = 0.736$, we can evaluate the contribution of the correlation effect to the nonbasal jump activation energy of self-diffusion at $1000/RT = 1$; thus

$$C_{A0} = R \; \frac{\partial \ln f_{A,z;0}}{\partial(1/T)} \; = - 0.154 \, \text{kcal/mole} . \quad (13)$$

For impurity diffusion, we can follow the same procedures outlined by Ghate[14] and evaluate

$$C_A = R \; \frac{\partial \ln f_{A,z}}{\partial(1/T)} \; . \quad (14)$$

The experimental results which have been used to determine the frequency ratios are as follows:

Cd(self-diffusion), $\ln A_{\parallel,0} = - 2.4$,

In$(Z = + 1)$, $\ln A_{\parallel} = - 2.29$,

Ag$(Z = - 1)$, $\ln A_{\parallel} = 0.34$,

Au$(Z = - 1)$, $\ln A_{\parallel} = 0.34$,

where A's are written for the D_0's and are in units of cm^2/sec. Then the theoretical calculation gives the following results:

ΔC_A (In in Cd) $= - 1.930$ kcal/mole ,

ΔC_A(Ag, Au in Cd) $= 0.310$ kcal/mole .

From Eq. (1) we obtain

$\Delta Q_{\parallel \text{theoret}}$ (In) $= - 1.600$ kcal/mole,

$\Delta Q_{\parallel \text{theoret}}$ (Au, Ag) $= 6.01$ kcal/mole .

The experimental values are

$\Delta Q_{\parallel \text{expt}}$ (In) $= - 1.16$ kcal/mole ,

$\Delta Q_{\parallel \text{expt}}$ (Ag) $= 6.03$ kcal/mole ,

$\Delta Q_{\parallel \text{expt}}$ (Au) $= 6.86$ kcal/mole .

2. Impurity Diffusion in Perpendicular Direction

One can deduce the following equations:

$$Y_{\parallel} = \frac{D_{\parallel}}{f_{A,z}} = \frac{1}{16} c^2 \nu_A \exp\left(\frac{\delta S_A}{R} \right) \exp\left(- \frac{E_A + H_A}{RT} \right), \quad (15)$$

$$Y_\perp = D_\perp - \frac{2a^2}{3c^2} \frac{(f_{A,b}/f_{A,z}) D_{\parallel}}{f_{B,x}}$$

$$= \frac{1}{8} a^2 \nu_B \exp\left(\frac{\delta S_B}{R} \right) \exp\left(- \frac{E_B + H_B}{RT} \right) . \quad (16)$$

Note that, if the Y's are plotted vs $1/T$, the energies $E_A + H_A$ and $E_B + H_B$ can be obtained from Eqs. (15) and (16). These values, which are taken as the experimental results, are next compared with the theoretical results.

In order to evaluate the Y's, correlation factors for different temperatures must be derived. The correlation factors can be obtained by solving Eqs. (9)–(11). The results are shown in Tables V and VI.

The energies obtained from the plots of the Y's vs $1000/RT$ are as follows:

In: $E_B + H_B = 14.260$ kcal/mole ,

$E_A + H_A = 14.320$ kcal/mole ;

Ag: $E_B + H_B = 25.880$ kcal/mole ,

$E_A + H_A = 24.680$ kcal/mole ;

Au: $E_B + H_B = 25.980$ kcal/mole ,

$E_A + H_A = 25.420$ kcal/mole .

By the same method, the following results for Cd self-diffusion were obtained:

$E_{A0} + H_{A0} = 18.440$ kcal/mole,

$E_{B0} + H_{B0} = 20.230$ kcal/mole .

An alternative way to estimate the theoretical value of Q for $Z = - 1$ is, after Ghate, as follows. Assume $\nu_A = \nu_B = \nu$, $\delta S_A = \delta S_B$, and $f_{B,x} = f_{A,b} = 1$. Then Eq. (16) becomes

$$D_\perp = \frac{1}{24} a^2 \nu \exp(\delta S/R)\{3 \exp[- (H_B + E_B)/RT]$$

$$+ \exp[- (H_A + E_A)/RT]\} .$$

Then, by assuming

$$(E_B + H_B)_{\text{theoret}} = (E_{B0} + H_{B0})_{\text{expt}} + (\Delta E_B + \Delta H_B)_{\text{theoret}}$$

$$= 30.460 \text{ kcal/mole} ,$$

$$(E_A + H_A)_{\text{theoret}} = (E_{A0} + H_{A0})_{\text{expt}} + (\Delta E_A + \Delta H_A)_{\text{theoret}}$$

$$= 24.660 \text{ kcal/mole} ,$$

one obtains

$$D_\perp = \frac{1}{24} a^2 \nu \exp[\delta S/R_e - 24.660(1000/RT)]$$

$$\times \{1 + 3 \exp[- 5.790(1000/RT)]\}$$

Evaluating the quantity in curly brackets at three temperatures one obtains values that differ

TABLE VI. Correlation factors pertaining to the diffusion of the Ag and Au tracer.

$1000/RT$	$f_{A,z}$	$f_{A,b}$	$f_{B,x}$
0.90	0.982	0.987	0.997
1.05	0.992	0.993	0.999
1.20	0.996	0.997	0.999

from 1 by only about 1%. Therefore, the contribution of the nonbasal jumps to the perpendicular diffusion is predominant, and the activation energy of the perpendicular diffusion is approximately equal to that of the parallel diffusion. Hence we have

$$Q_{\perp\,\mathrm{theoret}} \cong Q_{\parallel\,\mathrm{theoret}} = E_A + H_A = 24.660 \text{ kcal/mole} .$$

B. LeClair's Homovalent Diffusion Theory

When solute and solvent have the same valence ($Z = 0$), the differences in ionic size and differences in electronic constitution of ion cores are the only factors which contribute to the value ΔQ. Because size effects have been suggested as another manifestation of the perturbation potential $V(r)$ around an impurity, LeClaire attributed these ΔQ values directly to differences in the core potential of solvent and solute. It has been shown that these potentials can be estimated, for divalent metals, by the equation

$$E^0 = -\tfrac{1}{2}(H + 2F + I) , \qquad (17)$$

where H is the heat of sublimation (since no value of H is available for Zn, Cd, and Hg, the latent heat of vaporization is used as an approximation), F is the mean Fermi energy per electron,

$$F = \tfrac{3}{5} E_m ,$$

and I is the sum of the first and second ionization potentials. The impurity is represented by a square well of depth U, where $U = E_A^0 - E_B^0$, the subscripts A and B referring to the solvent and the solute atoms. The effect of the potential well is a redistribution of charge in its immediate surroundings, which gives a homovalent solute atom the same potential as a heterovalent solute atom of excess charge Z given by

$$(Z\alpha)_{\mathrm{eff}} = -(U/2qe^2)(qR - 1)\exp(qR) ; \qquad (18)$$

here R is the radius of the Wigner-Seitz sphere of the solvent metal. However, in reality, the size of the atom cell will change with the size of the impurity. I calculate the $(Z\alpha)_{\mathrm{eff}}$ values using the following choices for R: (1) the atomic radius of the solvent (used by LeClaire), (2) the radius

of the Wigner-Seitz sphere of the solvent metal, and (3) the radius of the compressed impurity atom, respectively, for four cases: Cd and Hg in Zn and Hg in Cd. The results are shown in Table VII. From Eqs. (3)–(5) we know that the ΔQ's should be proportional to $(Z\alpha)_{\mathrm{eff}}$ with an opposite sign. For the homovalent impurities in Cd even the sign is wrong.

V. DISCUSSION

A. Cadmium Self-Diffusion

The present investigation began when it was noticed that, in comparison with zinc, the diffusion constant is less anisotropic, although the c/a ratio is greater for cadmium. Mechanical methods for single-crystal orientation are of questionable value for cadmium since the metal is so ductile that the tip of a single cadmium crystal cannot be cleaved even at liquid-nitrogen temperature. Wajda et al.[3] used for their determination of orientation a "punching" method—observing slip-band patterns in the neighborhood of an indentation mark. After practicing this method and checking with an accurate x-ray Laue back-reflection method, it was found to be very difficult to achieve a 5° accuracy in most cases. Therefore, I suspect that the previously reported small anisotropy in Cd self-diffusion could be due to errors in the determination of specimen orientation.

The present experimental result showed a larger anisotropy with a small temperature dependence ($D_\perp/D_\parallel = 0.47-0.66$). As in the earlier investigation,[3] the difference in activation energy for $D_\parallel$ and $D_\perp$ is about 1 kcal/mole. Under these circumstances, numerous mechanisms would be able to explain the data. However, in the case of the zinc system the impurity-diffusion data have been satisfactorily interpreted in terms of the basal and nonbasal vacancy mechanisms. Measurements of the isotope effect in the zinc matrix also establish that vacancy (basal and nonbasal) mechanisms are the dominant mechanisms for diffusion in zinc. From many similar experimental results reported in this paper, one is tempted to assume that analogous mechanisms are at work in cadmium.

TABLE VII. Estimate of $(Z\alpha)_{\mathrm{eff}}$ for homovalent impurities in Zn and Cd. (All energies in kcal/mole.)

	$Q_\parallel$	Q	$\Delta Q_\parallel$	ΔQ	U	(1)	$(Z\alpha)$ (2)	(3)
Zn in Zn[49]	21.90	23.00						
Cd in Zn[58]	20.54	20.42	−1.36	−2.58	−41.511	+0.72	+1.36	+1.06
Hg in Zn[59]	19.70	20.18	−2.2	−2.82	−19.924	+0.33	+0.65	+0.48
Zn in Cd	18.03	18.02	−0.58	−1.57	41.511	−0.91	−1.77	−0.79
Cd in Cd	18.61	19.59						
Hg in Cd	18.78	18.78	+0.17	−0.81	21.587	−0.48	−0.92	−0.55

TABLE VIII. Comparison of theoretical and experimental results for impurity diffusion in Cd. (All energies in unit of kcal/mole.)

	$(\Delta E_A + \Delta H_A)_{expt}$	$(\Delta E_A + H_A)_{theoret}$	$(\Delta E_B + H_B)_{expt}$	$(\Delta E_B + H_B)_{theoret}$	$\Delta Q_{\parallel\ expt}$	$\Delta Q_{\parallel\ theoret}$	$\Delta Q_{\perp\ expt}$	$\Delta Q_{\perp\ theoret}$
In	-4.186	-3.533	-5.907	-5.807	-1.16	-1.60	-2.65	
Ag	$+6.233$	$+6.223$	$+5.649$	$+10.230$	$+6.03$	$+6.01$	$+5.48$	$+5.08$
Au	$+6.976$	$+6.223$	$+5.745$	$+10.230$	$+6.86$	$+6.01$	$+6.84$	$+5.08$

B. Heterovalent Diffusion

The general pattern of the diffusion results for heterovalent impurity diffusion (In, Ag, Au) in cadmium closely resembles that in zinc. One naturally is led to LeClaire's screening model[10] and its application to the hcp matrix by Ghate.[17] A summary of the final calculation results based on LeClaire's model is shown in Table VIII.

1. Diffusion of Indium

The excellent agreement between the experimental results and the theoretical calculations lends convincing support for the screening model. A main feature is the large contribution for positive Z solutes that comes from the temperature dependence of the correlation factor; for In in Cd, $\Delta C_A = -1.93$ kcal/mole for the nonbasal jump. From Table V, one notes that the correlation factors $f_{A,z}$, $f_{A,b}$, and $f_{B,x}$ are all very small, and the relation $f_{A,z} > f_{A,b} > f_{B,x}$ maintains. This indicates that the motion of the indium atom is highly correlated, and the correlation effect is much stronger in the basal direction. This result apparently stems from the assumption in this model that there is a strong attraction between the indium atom and the vacancy. When the temperature increases, thermal agitation randomizes this process and the correlation factor increases.

On the other hand, one notices that both C_{A0} and C_A will increase as the temperature increases. The effect will be larger for C_A because of a larger exponential term. Thus, the term C_A will probably increase slightly with temperature. However, the straight-line experimental results of the plots of $\ln D$ vs $1/T$ indicate constant diffusion activation energies. It is conceivable that some compensating effects exist or that the temperature effect of the C's is just too insignificant to be observed.

The results for parallel diffusion of In in Cd are

$$(\Delta Q_{\parallel})_{expt} = -1.16 \text{ kcal/mole} ,$$

$$(\Delta Q_{\parallel})_{theoret} = -1.60 \text{ kcal/mole} .$$

The agreement is almost within the experimental errors.

For the diffusion process perpendicular to the c axis, there are two types of jumps involved. Therefore, instead of directly comparing the activation energy, we have estimated the experimen-

tal value of $E_B + H_B$ from the calculated correlation factors and experimental diffusion coefficients. Obviously, the $E_{B0} + H_{B0}$ value for self-diffusion can be obtained by the same method. Then the difference is compared with the theoretically evaluated $\Delta E_B + \Delta H_B$. The results are

$$(\Delta E_B + \Delta H_B)_{expt} = -5.907 \text{ kcal/mole} ,$$

$$(\Delta E_B + \Delta H_B)_{theoret} = -5.807 \text{ kcal/mole} .$$

With a similar method, one can compare $\Delta E_A + \Delta H_A$ for the nonbasal jump. The results are

$$(\Delta E_A + \Delta H_A)_{expt} = -4.186 \text{ kcal/mole} ,$$

$$(\Delta E_A + \Delta H_A)_{theoret} = -3.533 \text{ kcal/mole} .$$

From these results, one sees that the agreement is really very good, perhaps fortuitously so.

2. Diffusion of Ag and Au

In the plot of $\ln D$ vs $1/T$ for silver in cadmium some upward curvature is apparent. We were at first tempted to consider this as evidence of short-circuiting dislocation paths which would enhance the low-temperature diffusivity according to the Hart model,[27] later modified by Mortlock[28] for impurity diffusion. Although it turned out that the extra diffusivity showed an activation energy consistent with grain boundary diffusion, several other considerations finally convinced us that it would be more realistic to forego reliance on a dislocation mechanism. Among these were the following.

(1) There is a lack of evidence for comparable dislocation effects for Au in Cd or Ag and Au in Zn.

(2) Data curvature gave a rms scatter only slightly larger than those in the other plots.

(3) Data fitting to a dislocation component would involve greater anisotropy in the Q values for the bulk process than would be simply explainable by a vacancy mechanism.

Therefore, I shall use the original set of data for Ag (Table II) for further consideration. By an analysis similar to In in Cd, we obtain the following results for Ag and Au diffusion in Cd:

$$(\Delta Q_{\parallel})_{expt} = +6.03 \text{ kcal/mole} \quad (\text{Ag})$$

$$= +6.86 \text{ kcal/mole} \quad (\text{Au}) ,$$

$$(\Delta Q_{\parallel})_{theoret} = +6.01 \text{ kcal/mole} \quad (\text{Ag and Au}) ;$$

$(\Delta E_A + \Delta H_A)_{expt} = +6.233$ kcal/mole (Ag)

$= +6.976$ kcal/mole (Au),

$(\Delta E_A + \Delta H_A)_{theoret} = +6.223$ kcal/mole (Ag and Au);

$(\Delta E_B + \Delta H_B)_{expt} = +5.649$ kcal/mole (Ag)

$= +5.745$ kcal/mole (Au),

$(\Delta E_B + \Delta H_B)_{theoret} = +10.230$ kcal/mole (Ag and Au).

Again, the agreement is within the experimental errors, except for the case of $\Delta E_B + \Delta H_B$. The relatively larger discrepancy in the values of $\Delta E_B + \Delta H_B$ may be due to the possibility that the correct Z value is more positive than -1, so that a value of $Z = -1$ leads to an overestimation of $(\Delta E_B + \Delta H_B)_{theoret}$. This term is most sensitive to the Z value because of the close distance between the impurity atom and vacancy in this configuration.

An alternative approach, following Ghate, is to estimate the $Q_{theoret}$ value on the basis that the contribution to perpendicular diffusion is still largely due to the nonbasal jump; this gives a value

$Q_{theoret} = 5.08$ kcal/mole (Ag, Au in Cd).

The theoretical and experimental values again agree very well. On examination of Table VI, one finds that the sequence $f_{A,z} < f_{A,b} < f_{B,x} \cong 1$ holds. This indicates that, just opposite to the indium case, the motion for a $Z = -1$ impurity atom is very weakly correlated with a slight anisotropy favoring the parallel direction. This anisotropy cannot account for the large anisotropy observed in the impurity Ag diffusing in Cd. There is a tendency to attribute this to a size effect,[12] where the movement of large atoms is probably impeded in the close-packed basal planes more than in plane-to-plane motion.

One of the peculiar features in which impurity diffusion in Cd is different from that in Zn is the very small anisotropy found for diffusion of Au in Cd. Gold and silver have almost identical atomic radii, so the size effect cannot be dominant. However, it has been shown by Kambe[29] that the discrepancy between the electrostatic cohesion calculated from interactions between the s-valence electrons and positive-ion cores and the experimental cohesive energy is greatest for gold and smallest for silver of the pure noble metals, indicating perhaps that van der Waals forces are highest between gold-ion cores and smallest between silver-ion cores. It is claimed that a similar effect exists between the solute and the solvent ion cores, when the solute is isoelectronic with a noble-metal ion, for a separation of the order of the nearest-neighbor distance in the pure noble metals.[30] This condition is fulfilled for the Au atom in cadmium, but is not satisfied for the Au atom in zinc because of the larger size difference between Zn and Au atoms. The presence of the van der Waals type of force

for the gold atom modifies its size effect in cadmium, thereby greatly reducing the anisotropy of the movement of the Au atom in the Cd matrix by increasing the contribution from the basal jumps.

In general, LeClaire's modified screening model provides a satisfactory explanation of heterovalent diffusion in cadmium. If one plots the activation energy for the perpendicular direction as a function of valence difference, one finds that for Ag and Au the Z value gives a better fit if it lies between -1 and 0 (≈ -0.63). This adaptation is in line with the treatment for Ag and Au diffusion in zinc; because of the closer interaction distances the energies for the basal configuration are affected more by the choice of Z than those for the A jumps.

C. Homovalent Diffusion

While LeClaire's heterovalent theory[21] has been successfully applied for the impurities In, Ag, and Au diffusing in cadmium, the situation is not so fortunate with LeClaire's homovalent theory. In fact, the difficulty involved in applying this theory has already been encountered in the case of zinc, as follows.

First we plot the activation energy difference vs the $Z\alpha$ value for the parallel direction (only nonbasal jumps are involved) for impurities Cu, Ag, Au, Ga, and In diffusing in Zn. For the activation energies measured experimentally for Cd and Hg diffusing in Zn to agree with this screening model would require that

$(Z\alpha)_{eff} \cong +0.35$ (for Cd),

$(Z\alpha)_{eff} \cong +0.55$ (for Hg).

However, based on LeClaire's estimate, one gets

$(Z\alpha)_{eff} = +0.72$ (for Cd),

$(Z\alpha)_{eff} = +0.33$ (for Hg).

Here, as shown in Table VII, the quantity $(Z\alpha)_{eff}$ is very sensitive to the value which one takes for R (the radius of the Wigner-Seitz sphere). Just by changing R, however, the relative magnitude between Cd and Hg can hardly be changed. One might also question the method used to estimate U, since it ignores all the exchange, correlation, and Coulomb contributions to the cohesive energy. These contributions nearly cancel each other completely for monovalent metals, but there is no near cancellation for polyvalent metals.

A similar comparison for impurity diffusion in cadmium gives following results.

Experimental results require

$(Z\alpha)_{eff} = +0.25$ (Zn), $(Z\alpha)_{eff} \cong 0$ (Hg);

theoretical estimate requires

$(Z\alpha)_{eff} = -0.91$ (Zn) , $(Z\alpha)_{eff} = -0.48$ (Hg) .

The relative magnitude between Zn and Hg is again inverted and the sign of the theoretical estimate is also opposite to that observed experimentally.

One way to rationalize the present results is to introduce the size effect which has been previously neglected. For impurity diffusion in Zn, one observes the reversal of anisotropy of Cd diffusion and the small anisotropy for both Cd and Hg. One is led to speculate that the valence effect and size effect are competing influences. It seems that the valence effect is dominant in the Cd case, and the two effects are comparable in the case of Hg.

For impurity diffusion in Cd, the situation is a little different. The diffusion of Hg is isotropic within experimental error (slightly larger in the perpendicular direction), and Zn diffusion shows no reversal in anisotropy although it diffuses faster than Cd self-diffusion. This indicates that size-effect considerations may be important. Therefore, when I extended Swalin's simple elastic model to hcp metals using the Hg diffusion data to derive the geometrical constants, I obtained the following results for Zn diffusion:

$$Q_{\parallel \; theoret}(Zn) = 17.98 \; kcal/mole ,$$

$$Q_{\parallel \; expt} (Zn) = 18.03 \; kcal/mole .$$

One can see that the agreement is good. Owing to many approximations, this kind of calculation cannot be trusted too far. Indeed, when I carried this evaluation to heterovalent materials, I found no agreement. For perpendicular diffusion, I could not find an easy way to extend the model, mainly because two kinds of jumps are involved in this case. The point which I stress here is that, for homovalent diffusion in divalent metals, the size of ion core could be as important as the effect of core potential. I have demonstrated that by using various simple models I can get numbers which agree satisfactorily with the experimental results individually, but this is not the same as a generally consistent theory which can explain all these facts.

D. Isotope Effect of Zn in Cd

Two runs at different temperatures were made to study the relative diffusivities of Zn^{65} and Zn^{69m} in cadmium, but only for the run at 199.3 °C was the quality of data (Fig. 8) sufficiently reliable to warrant reporting. The values for $D^{65}/D^{69} - 1$ and E^{65}_{69m} are given in Table III. The limits of error are still appreciably larger than what is generally possible with current techniques.

The difficulties which we encountered in the isotope experiments are mainly the maintenance of a stable counting system and the prevention of sur-face holdup. The phenomenon of surface oxidation presented the most difficult problem in a large number of our early runs for zinc diffusion in cadmium. It was finally overcome by improving the vacuum of the annealing capsule, using fresh isotope for each plating, eliminating the dead zinc content in the plating bath, and lightly etching the samples immediately before plating. It seems apparent that the near-surface effect caused troubles in earlier diffusion data of zinc in cadmium.

The purpose of the isotope measurements was mainly to determine whether the interstitial mechanism was operating in the case of diffusion of zinc in cadmium. If the zinc impurity is located at an interstitial position, then one can explain why Zn diffuses faster than self-diffusion, although one would probably run into another dilemma in the explanation of the nonreversal of the anisotropy.

A comparison of the experimental values for $D_{\parallel}$ and $D_{\perp}$ for Zn in Cd with the corresponding predictions from the various diffusion mechanisms makes it evident that the interstitial mechanism cannot be operating alone. However, it is also true that an unambiguous identification of mechanisms for diffusion cannot be made. The fact that the E values from the isotope experiment are appreciably less than 1 substantiates the general feeling, based on the impurity studies, that diffusion in cadmium does not appreciably involve the interstitial mechanism.

The anisotropy of the double-isotope studies shows E parallel to the hexagonal lattice to be less than E for diffusion in the basal plane. This is in the direction that one would expect from $E = f(\Delta K)$, where ΔK is the "energy sharing factor." Since $D_{\parallel} > D_{\perp}$, for Zn in Cd, one would expect $f_{\parallel} < f_{\perp}$. Presumably ΔK, like the activation volume ΔV,[31] is relatively isotropic.

VI. CONCLUSIONS

(1) The heterovalent impurity diffusions in cadmium agree with evaluations calculated from the LeClaire's version of the electrostatic interaction theory. It indicates that the valence effect is indeed playing a dominant role in diffusion.

(2) The impurity diffusion data of Ag in Cd indicate that there is a possibility of dislocation enhancement. However, I feel more confident that the Ag-diffusion data represent primarily bulk diffusion.

(3) The small anisotropy of diffusion of Au in Cd might indicate the existence of a van der Waals-type force which has not been observed for Au diffusion in Zn.

(4) The fast diffusion of Zn in Cd can be explained to a certain extent by a size effect. This agrees with the finding of Zn-isotope experiments. The previously reported low-diffusion coefficients for Zn are probably in error.

(5) There is a large increase in D in going from noble metals to polyvalent metals diffusing in Cd. This increase is more prominent than the case of impurity diffusion in Zn.

(6) The consistent picture presented by the impurity diffusion in Cd leads us to believe that the vacancy is indeed the main operating mechanism. There are cases where the size considerations may dominate the diffusion energetics and other cases where it may affect the anisotropy.

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Lattice-Constant Dependence on Isotopic Composition in the ⁷Li(H, D) System*

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Initial measurements of the lattice constant by neutron diffraction for two compositions in the Li (H, D) system have indicated a nonlinear behavior. To delineate this variation more clearly, analysis of twelve compositions has been performed by x-ray diffraction. The Debye-Scherrer powder method is used, and the film is positioned in the Straumanis manner. The lattice constants are calculated by the Nelson-Riley extrapolation method with Cohen's least-squares analysis. If impurities are present (mostly Li_2O and LiOH), it is found that the variation with isotopic composition does tend to be nonlinear. However, upon removal of practically all impurities, the variation becomes essentially linear between the two extremes of ⁷LiH and ⁷LiD, in agreement with Vegard's law.

I. INTRODUCTION

The large relative mass difference between the H and D isotopes makes the Li(H, D) system an interesting one to study. Since the system has the NaCl-type structure, it is one of the simpler crystal lattices. The dependence of the infrared dispersion frequency on isotopic composition in the Li-(H, D) system has been investigated experimentally[1,2] and analyzed theoretically.[3] The relation was