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Diffusion of lead in cadmium

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The anisotropic diffusion coefficients of ^{210}Pb in single crystals of cadmium have been measured by the tracer-sectioning method. The results of the measurements are $D_{\parallel} = (0.060 \pm 0.024)\exp[-(16.46 \pm 0.44 \text{ kcal/mole})/RT]$, $D_{\perp} = (0.071 \pm 0.012)\exp[-(15.71 \pm 0.19 \text{ kcal/mole})/RT]$, all in cm^2/sec. This study of the diffusion of a quadrivalent impurity in cadmium supplements an earlier investigation of the diffusion of mono-, di-, and trivalent atoms in the same matrix. The activation energies obtained in this study can be interpreted with LeClaire's screening model. Fair agreement between the experimental results and theoretical calculations are obtained. It indicates that the valence effect is indeed playing a dominant role in diffusion.

I. INTRODUCTION

The electrostatic-interaction theory proposed by Lazarus[1] and later refined by LeClaire[2,3] has been proved successful in explaining the overall pattern for impurity diffusion in fcc noble metals and hcp zinc and cadmium. The theory is based on the electrostatic interaction between a screened impurity and its neighboring vacancy. For the hcp structure solvent, the general trend of the activation energy with the valence of the diffusing solute lends support to the assumption that the diffusion is taking place via basal and nonbasal vacancy mechanisms. The monovalent-, divalent-, and trivalent-impurity diffusions in single-crystal cadmium have been measured in this laboratory.[4] The results agree well with the evaluations calculated from LeClaire's theory and with the correlation factors in anisotropic material developed by Huntington and Ghate.[5] It indicates that the valence effect is indeed playing a dominant role in diffusion. With the intention of extending the study to a quadrivalent impurity, it was decided to investigate the diffusion of lead as an impurity in cadmium.

II. EXPERIMENTAL TECHNIQUE

The procedure employed for sample preparation was similar to that described elsewhere.[6] Single crystals of cadmium were grown by the Bridgman method from 99.999% pure cadmium obtained from Cominco American, Inc. Diffusion samples $\frac{1}{2}$ inch in diameter were cut by a specially designed multiple-string saw into $\frac{3}{8}$-inch lengths. Their orientations were determined by the Laue back-reflection method. Only those crystals which had their cylindrical axes closely parallel or perpendicular to the hexagonal axis were retained for the experimental work.

The radioisotope ^{210}Pb was supplied by New England Nuclear Corp. in nitric acid solution. The plating bath for the deposition consisted of 100 cm^3 H_2O, 6.0 g KCN, and 4.5 g K_2CO_3. Pure platinum was used as the anode in the electroplating bath. A current density of about 20 mA/cm^2 was used during electroplating. The plating time was about 30 min to insure that over 10 000 counts/min of surface activity was detected with a survey meter. This high initial activity was necessary in order to get good statistics with a reasonable counting time.

The sample was vacuum sealed in a Pyrex capsule. The diffusion runs were performed in the temperature range from 240 to 298 °C with diffusion anneals lasting from three hours to five days. The temperature was controlled to within ±0.5 °C over these periods. After each run, the monitoring thermocouple was calibrated against a National Bureau of Standards standardized platinum (platinum 10 at.% rhodium) thermocouple. Warm-up corrections[7] were applied in computing the time of the diffusion anneal. The capsule was quenched in ice water after each run. After the diffusion anneals, the diffusion coefficients were obtained by the standard lathe-sectioning and radioactive-counting techniques.[8]

III. RESULTS

A typical penetration profile is shown in Fig. 1, where the logarithm of the specific activity is plotted as a function of the square of the penetration distance. The diffusion constants, parallel to c axis $D_{\parallel}$ and perpendicular to c axis $D_{\perp}$, were obtained by solving the two simultaneous equations for runs at the same temperature:

$$D(\theta_1) = D_{\parallel}\cos^2\theta_1 + D_{\perp}\sin^2\theta_1 , \tag{1}$$

$$D(\theta_2) = D_{\parallel}\cos^2\theta_2 + D_{\perp}\sin^2\theta_2 . \tag{2}$$

The values for θ_1, θ_2, $D(\theta_1)$, $D(\theta_2)$, $D_{\parallel}$, and $D_{\perp}$ are listed in Table I. In Fig. 2, the logarithms of the diffusion coefficient for both orientation are plot-

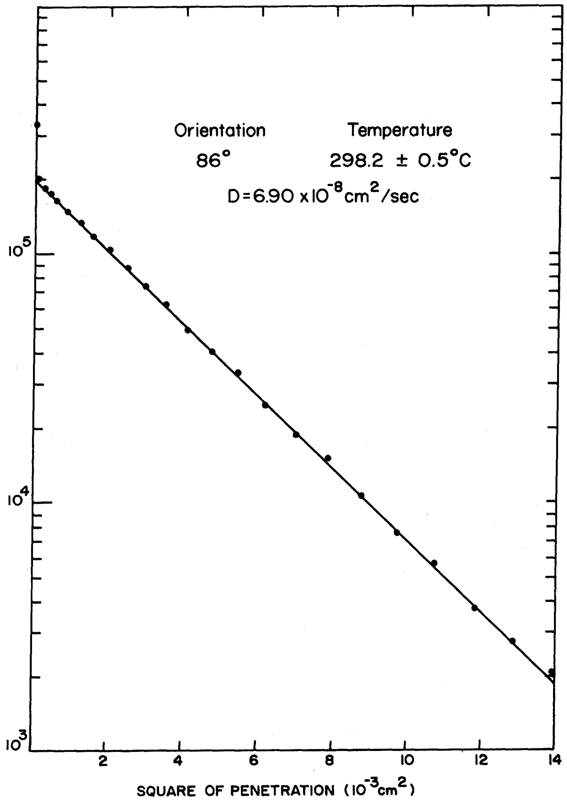

FIG. 1. Penetration profile for diffusion of Pb in Cd.

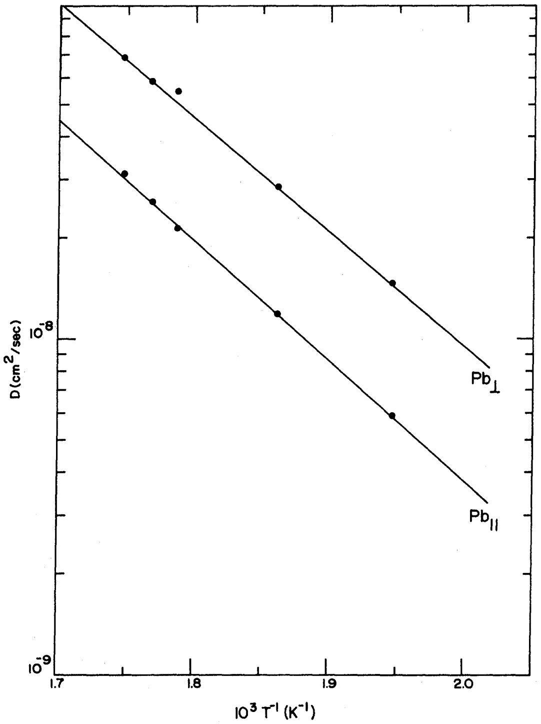

FIG. 2. Temperature dependence of D for diffusion of Pb in Cd.

ted versus the reciprocal temperature. The temperature dependence of the diffusion coefficients can be expressed as

$$D_\parallel = (0.060 \pm 0.024) \times \exp[-(16.46 \pm 0.44\ \text{kcal/mole})/RT]\ \text{cm}^2/\text{sec}\,, \tag{3}$$

$$D_\perp = (0.071 \pm 0.012) \times \exp[-(15.71 \pm 0.19\ \text{kcal/mole})RT\,]\,\text{cm}^2/\text{sec}. \tag{4}$$

The parameters of the above equations, obtained from least-squares analysis,[9] are shown in Table II. The Arrhenius plots for the diffusion of different impurities obtained in the earlier investigations are included in Fig. 3 for comparison. The

TABLE I. Diffusion coefficient of Pb in Cd at various temperatures.

Temperature	Orientation	D (cm^2/sec)	$D_\parallel$ (cm^2/sec)	$D_\perp$ (cm^2/sec)	$D_\parallel/D_\perp$
240.5 °C	6° 86°	$(5.98 \pm 0.29) \times 10^{-9}$ $(1.45 \pm 0.02) \times 10^{-8}$	$(5.89 \pm 0.29) \times 10^{-9}$	$(1.45 \pm 0.02) \times 10^{-8}$	0.41
263.8 °C	18° 86°	$(1.35 \pm 0.02) \times 10^{-8}$ $(2.82 \pm 0.05) \times 10^{-8}$	$(1.19 \pm 0.02) \times 10^{-8}$	$(2.82 \pm 0.05) \times 10^{-8}$	0.42
285.9 °C	18° 84°	$(2.46 \pm 0.05) \times 10^{-8}$ $(5.40 \pm 0.10) \times 10^{-8}$	$(2.15 \pm 0.04) \times 10^{-8}$	$(5.44 \pm 0.10) \times 10^{-8}$	0.40
291.8 °C	6° 84°	$(2.61 \pm 0.09) \times 10^{-8}$ $(5.78 \pm 0.07) \times 10^{-8}$	$(2.57 \pm 0.09) \times 10^{-8}$	$(5.82 \pm 0.08) \times 10^{-8}$	0.44
298.2 °C	1° 86°	$(3.12 \pm 0.14) \times 10^{-8}$ $(6.90 \pm 0.09) \times 10^{-8}$	$(3.12 \pm 0.14) \times 10^{-8}$	$(6.92 \pm 0.09) \times 10^{-8}$	0.45

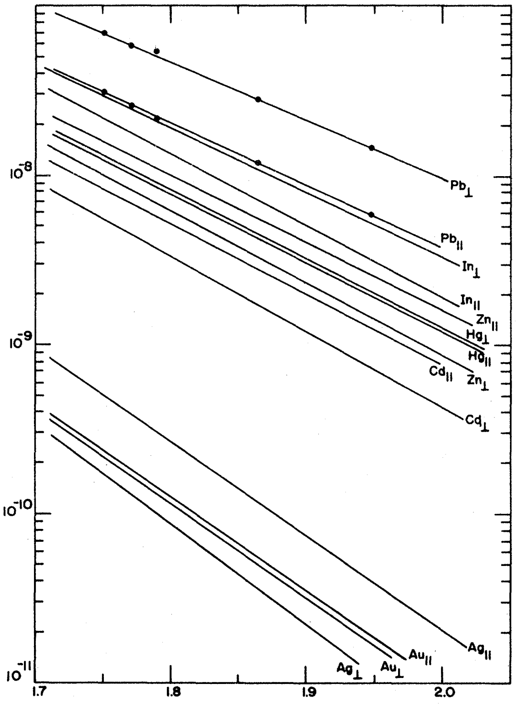

FIG. 3. Temperature dependence of D for impurity diffusion in Cd.

other parameters of the diffusion of different impurities in cadmium are also listed in Table II for comparison. A definite correlation between ΔQ and ΔZ can be seen in Fig. 4. The general appearance of this figure is reminiscent of a similar plot for impurity diffusion in zinc as presented by Warford.[10]

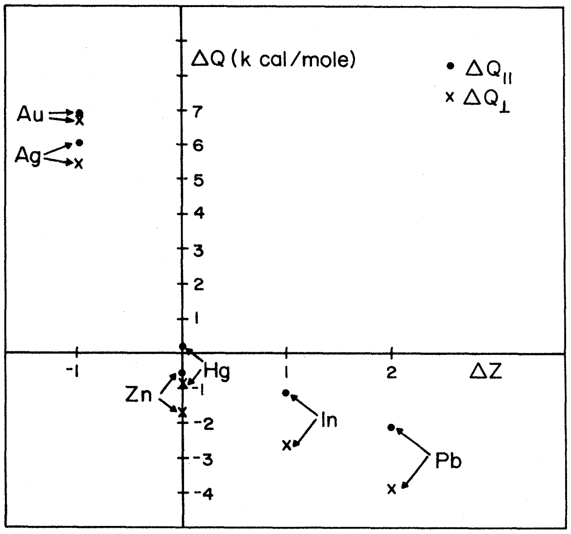

FIG. 4. Correlations with valence difference ΔZ and the changes in activation energies for various impurities from that for the self-diffusion of Cd.

IV. APPLICATION OF THEORY

In LeClaire's theory a free-electron model for the pure metal is assumed with positive ion cores smeared out to give a uniform positive charge density. An impurity is treated as a point charge which is screened by an excess of electronic charge if $\Delta Z > 0$ and by a deficit of charge if $\Delta Z < 0$. The Thomas-Fermi model is used to calculate the potential:

$$V(r) = \alpha \frac{\Delta Z e}{r} \exp(-qr) , \qquad (5)$$

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

Solute	ΔZ	$\ln D_{0\parallel}$ (cm²/sec)	$\ln D_{0\perp}$ (cm²/sec)	$Q_\parallel$ (kcal/mole)	$Q_\perp$ (kcal/mole)	$D_\parallel/D_\perp$
Au	−1	0.34 ± 0.08	1.15 ± 0.02	25.47 ± 0.08	26.43 ± 0.02	
Ag	−1	0.34 ± 0.47	−0.39 ± 0.62	24.64 ± 0.48	25.07 ± 0.65	
Hg	0	−1.55 ± 0.07	−1.55 ± 0.07	18.78 ± 0.06	18.78 ± 0.06	
Cd	0	−2.14 ± 0.13	−1.70 ± 0.19	18.61 ± 0.12	19.59 ± 0.19	
Zn	0	−2.04 ± 0.26	−2.48 ± 0.24	18.03 ± 0.25	18.02 ± 0.24	
In	1	−2.29 ± 0.20	−2.41 ± 0.16	17.45 ± 0.19	16.94 ± 0.15	
Pb	2	−2.82 ± 0.41	−2.65 ± 0.17	16.46 ± 0.44	15.71 ± 0.19	
		$\Delta \ln D_{0\parallel}$	$\Delta \ln D_{0\perp}$	$\Delta Q_\parallel$	$\Delta Q_\perp$	
Au	−1	2.48	2.85	6.86	6.84	1.12
Ag	−1	2.48	1.31	6.03	5.48	3.14
Hg	0	0.59	0.15	0.17	−0.81	0.96
Cd	0	0	0	0	0	1.63
Zn	0	0.10	−0.78	−0.58	−1.57	1.60
In	1	−0.15	−0.71	−1.16	−2.65	0.69
Pb	2	−0.68	−0.95	−2.15	−3.88	0.42

where q is the screening parameter characterized by the solvent, α is a constant depending on ΔZ only. For this case of the impurity Pb diffusing in Cd, $\Delta Z = 2$ and $\alpha = 1.344$ which was determined by using the master solution given by Umeda and Koboyashi.[11]

The difference in activation energy between self-diffusion and impurity diffusion is

$$\Delta Q = \Delta E + \Delta H - \Delta C \,, \tag{6}$$

where ΔE is the difference between the energy required to form a vacancy next to an impurity atom and the energy needed to form a vacancy in the pure solvent. ΔH 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 last term comes from the difference between the temperature dependence of the correlation factor for impurity difference and that for self-diffusion. The expression for C is

$$C = R \frac{\partial \ln f}{\partial (1/T)} \,, \tag{7}$$

where f is the corresponding correlation factor. For the divalent solvent, the expressions of ΔE and ΔH, are

$$\Delta E = -2 \text{ eV } (\lambda) \,, \tag{8}$$

$$\Delta H = -2 \text{ eV } (\tfrac{11}{16}\lambda) - \Delta E \,, \tag{9}$$

where λ is the jump distance, $\frac{11}{16}\lambda$ is the distance between the impurity and the centroids of the half-vacancy hemispheres that flank the impurity at the saddle point.

When setting the impurity atom at the origin O $(0,0,0)$ and the vacancy in the next plane A $(a/2, \sqrt{3}a/6, c/2)$, the various energies for A jump (nonbasal jump), in units of kcal/mole, are

$$\Delta E_A = -1.278 \,, \tag{10a}$$

$$\Delta H_A = -11.021 \,, \tag{10b}$$

$$\Delta H_{a'} = 0.380 \,, \tag{10c}$$

$$\Delta H_{b'} = 0.584 \,, \tag{10d}$$

$$\Delta H_{c'_{\text{av}}} = -0.0286 \,, \tag{10e}$$

where ΔE_A and ΔH_A are the same as ΔE and ΔH in Eq. (6). $\Delta H_{a'}$ is the change of the activation energy for the exchange of a vacancy neighboring a solute atom with a solvent atom that is also a neighbor of the solute and is in the same plane as the solute. $\Delta H_{b'}$ is the change of the activation energy for the exchange of a vacancy neighboring a solute atom with a solvent atom that is also a neighbor of the solute and is in the same plane as the vacancy. $H_{c'_{\text{av}}}$ is the average value of the change of the activation energy for the exchange of a vacancy neighboring a solute atom with a solvent atom which does not adjoin the solute. In this case, there are seven escape jumps which lead to four different values of activation energy change, the average value is evaluated as

$$\exp[-(\Delta H_{c'_{\text{av}}})/RT] = \tfrac{1}{7} \sum_i \exp(-\Delta H_{c'_i}/RT) \,. \tag{11}$$

The temperature used in the averaging calculation is 269.4 °C which is approximately the midpoint of the temperature range of diffusion measurements and corresponds to $1000/RT = 0.928$ mole/kcal.

For B jump (basal jump) the impurity atom is again set at O $(0,0,0)$ and the vacancy is set in the same plane B $(a,0,0)$, then the various associated energies, in kcal/mole, are

$$\Delta E_B = -2.517 \,, \tag{12a}$$

$$\Delta H_B = -17.708 \,, \tag{12b}$$

$$\Delta H_a = 1.619 \,, \tag{12c}$$

$$\Delta H_b = 1.240 \,, \tag{12d}$$

$$\Delta H_{c_{\text{av}}} = -0.216 \,. \tag{12e}$$

The calculation of $R\partial \ln f/\partial(1/T)$ requires knowledge of the correlation factor. The expression for the correlation factors in anisotropic material has been developed by Huntington and Ghate.[5] These values for the Cd self-diffusion and the diffusion of Pb in Cd are shown in Table III.

A. Impurity diffusion in parallel direction

The exponential dependence of D on temperature follows from kinetic theory. On an atomic scale, D

TABLE III. Correlation factors for the Cd self-diffusion and the diffusion of Pb in Cd.

$1000/T$	$f_{A,Z;0}$	$f_{A,b;0}$	$f_{B;0}$	$f_{A,Z}$	$f_{A,b}$	f_B
1.75	0.7655	0.6025	0.7993	0.2732	0.2608	0.1235×10^{-2}
1.80	0.7623	0.5991	0.8031	0.2215	0.2120	0.8173×10^{-3}
1.85	0.7591	0.5960	0.8069	0.1771	0.1692	0.5415×10^{-3}
1.90	0.7561	0.5932	0.8106	0.1401	0.1330	0.3591×10^{-3}
1.95	0.7531	0.5906	0.8143	0.1097	0.1032	0.2384×10^{-3}

is proportional to atom jump frequency. In hcp crystals with basal and nonbasal vacancy mechanisms, it can be shown[12,13] that

$$D_{\parallel}=\tfrac{1}{16}c^2\nu_A f_{A,z}\exp(\delta S_A/R)\exp[-(E_A+H_A)/RT], \tag{13}$$

$$D_{\perp}=\tfrac{1}{8}a^2 f_B\nu_B\exp(\delta S_B/R)\exp[-(E_B+H_B)/RT] + \tfrac{1}{24}a^2 f_{A,b}\nu_A\exp(\delta S_A/R)\exp[-(E_A+H_A)/RT], \tag{14}$$

where subscript A indicates quantities for nonbasal jump. This jump contribution has two components: one parallel to c axis indicated by subscript Z and one along the basal plane indicated by subscript b. Subscript B indicates quantities for the basal jump, ν the vibration frequency, δS the entropy factor, E the vacancy formation energy, H the vacancy migration energy, and f the correlation factor.

Following the same procedures outlined by Ghate[14] and using Cd self-diffusion experimental results obtained by Mao,[4] the theoretical calculation gives the result

$$\Delta C_A=R\frac{\partial\ln f_{A,z}}{\partial(1/T)}-R\frac{\partial\ln f_{A,z;0}}{\partial(1/T)} = -9.069+0.164=-8.905, \tag{15}$$

in units of kcal/mole, where subscript 0 indicates the self-diffusion. From Eqs. (6), (10a), and (10b) we have,

$$\Delta Q_{\parallel(\text{theor})}=-3.39, \tag{16}$$

in units of kcal/mole. The experimental values, also in units of kcal/mole, are

$$\Delta Q_{\parallel(\text{expt})}=-2.15. \tag{17}$$

Although the theory seems to overemphasize the effect of the impurity valence, the discrepancy is not too large considering the approximate nature of the theory.

B. Impurity diffusion in perpendicular direction

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 estimated the experimental value of the basal jump activation energy $Q_{\perp b}$ from the calculated correlation factor and experimental diffusion coefficients and then compared them with the theoretical calculated values obtained from Eqs. (6), (7), and (12).

From the Eqs. (13) and (14), we can deduce the following equation

$$\begin{aligned} D_{\perp b}&=\tfrac{1}{8}a^2 f_B\nu_B\exp(\delta S_B/R)\exp[-(E_B+H_B)/RT]\\ &=D_{\perp}-\tfrac{1}{24}a^2 f_{A,b}\nu_A\exp(\delta S_A/R)\exp[-(E_A+H_A)/RT]\\ &=D_{\perp}-2a^2 f_{Ab}D_{\parallel}/3c^2 f_{A,z}\,. \end{aligned} \tag{18}$$

With the values of correlation factors for different temperatures shown in Table III, Cd self-diffusion experimental results obtained by Mao,[4] and the present experimental results for $D_{\parallel}$ and $D_{\perp}$, the values of $D_{\perp b}$(Cd) and $D_{\perp b}$(Pb) for various temperatures can be calculated from Eq. (18).

Note that if we plot $D_{\perp b}$'s vs $1/T$ as shown in Fig. 5, the activation energy $Q_{\perp b}$'s can be obtained. These values, which are taken as the experimental results, can be compared with the theoretical results. The activation energies obtained from the plot of $D_{\perp b}$'s vs $1/T$ are as follows in kcal/mole:

$$Q_{\perp b}(\text{Cd})=19.88\,, \tag{19}$$

$$Q_{\perp b}(\text{Pb})=15.64\,. \tag{20}$$

Hence

$$\Delta Q_{\perp b(\text{expt})}=Q_{\perp b}(\text{Pb})-Q_{\perp b}(\text{Cd})=-4.24\,, \tag{21}$$

with units of kcal/mole. The theoretical calcula-

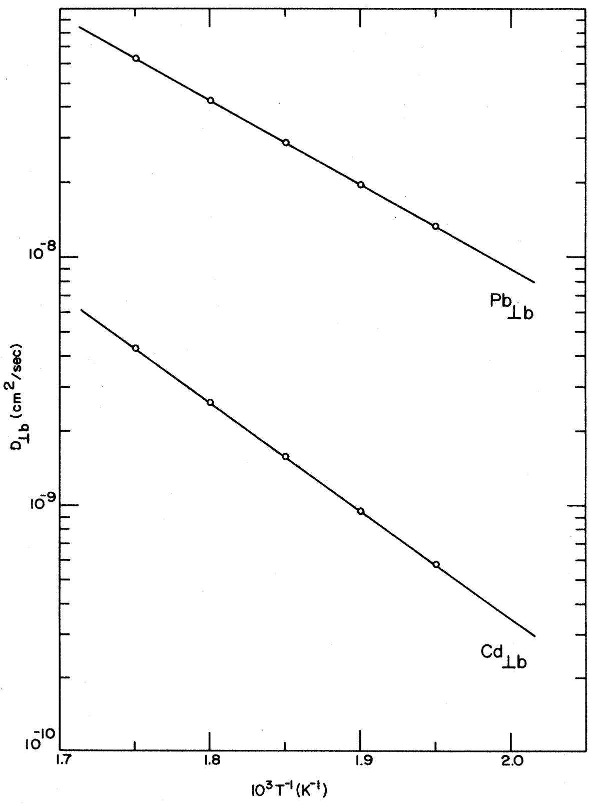

FIG. 5. Temperature dependence of $D_{\perp b}$ for the Cd self-diffusion and the diffusion of Pb in Cd.

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

	$\Delta Q_{\parallel \mathrm{expt}}$	$\Delta Q_{\parallel \mathrm{theor}}$	$\Delta Q_{\perp \mathrm{expt}}$	$\Delta Q_{\perp \mathrm{theor}}$	$\Delta Q_{\perp b\, \mathrm{expt}}$	$\Delta Q_{\perp b\, \mathrm{theor}}$
Au	6.86	6.01	6.84	5.08		
Ag	6.03	6.01	5.48	5.08		
In	−1.16	−1.60	−2.65			
Pb	−2.15	−3.39	−3.88		−4.24	−3.69

tion of the contribution of the correlation effect to the basal jump activation energy of the Cd self-diffusion, take $1000/RT = 0.928$ mole/kcal

$$C_{B;0} = R\,\frac{\partial \ln f_{B;0}}{\partial(1/T)} = 0.184\,. \tag{22}$$

For the diffusion of Pb in Cd, in units of kcal/mole,

$$C_B = R\,\frac{\partial \ln f_B}{\partial(1/T)} = -16.347\,. \tag{23}$$

Hence

$$\Delta C_B = -16.347 - 0.184 = -16.531\,. \tag{24}$$

From Eqs. (6) and (12a), and (12b) we have

$$\Delta Q_{\perp b(\mathrm{theor})} = -3.69\,, \tag{25}$$

where all C and Q values are expressed in kcal/mole.

V. DISCUSSION

A summary of the final calculation results based on LeClaire's screening model is shown in Table IV. Also shown in the same table for comparison are similar results obtained in earlier investigations of trivalent and monovalent impurities in Cd. The agreement between the experimental results and theoretical calculations lends convincing support for the screening model. It indicates that the valence effect is indeed playing a dominant role in diffusion. A main feature is the large contribution that comes from the temperature dependence of the correlation factor which is −8.905 kcal/mole for nonbasal jump and −16.531 kcal/mole for basal jump.

From Table III we can note that the correlation factors f_B are much smaller than $f_{A,z}$ and $f_{A,b}$. This indicates that the correlation effect is much stronger in the basal direction because there is frequent interchange of vacancy and Pb atom in the basal plane. When the temperature increases, the preference for basal jump becomes not quite so strong and the correlation factor increases.

On the other hand, one could notice from Fig. 3 that the diffusivity of Pb is found to be significantly greater than that of the trivalent impurity In. Furthermore, as Table II indicates, $D_\parallel/D_\perp$ of Pb is the smallest yet observed and the anisotropy of D is the greatest for impurity diffusion in Cd. The behavior of the ratio $D_\parallel/D_\perp$ can be explained by examining the c/a ratio in Cd. In a truly hexagonal-closed-packed lattice, diffusion takes place via the vacancy mechanism by two types of nearest-neighbor jumps. One is in the basal plane, B type, and one is from the basal plane to an adjacent basal plane, A type. However, the c/a ratio in cadmium ($c = 5.617$ Å, $a = 2.9787$ Å, $c/a = 1.89$) deviates from the close-packed value (about 1.63) by 16%. The c axis is elongated and the atoms in adjacent planes are no longer nearest neighbors. Hence, impurities with $\Delta Z > 0$ have a stronger attraction for vacancies in the same basal plane and $D_\perp$ becomes larger than $D_\parallel$.

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