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Temperature-Dependent Activation Volumes of Self-Diffusion in Cadmium*

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The principal-axis self-diffusion coefficients of cadmium were measured over the temperature range 250–320 °C and over the pressure range 0–8 kbar. The self-diffusion activation volumes of the basal and nonbasal vacancy mechanisms are found to be temperature dependent, isotropic, and approximately proportional to the absolute temperature. We find that the activation entropy has a pressure dependence of -0.011 ± 0.002 cm^3/mole °K, whereas the activation enthalpy is independent of pressure within our experimental uncertainty.

I. INTRODUCTION

It has been established that self-diffusion in cadmium occurs by two single-vacancy mechanisms. By comparing macroscopic thermal expansion to microscopic (x-ray) thermal expansion, Feder and Nowick[1] have concluded that monovacancies are the thermally generated defects in cadmium. Studies of self-diffusion[2,3] and impurity diffusion[3] as well as an impurity-isotope-effect measurement[3] have shown that the two vacancy mechanisms responsible for diffusion are jumps within and jumps out of the basal plane.

The ratio of the diffusion coefficient in the c direction, D_c, to that in the basal plane, D_b, is approximately 2, and the activation energies differ by about 7%. The linear isothermal compressibilities of cadmium in the c- and a-axis directions differ by about an order of magnitude. These anisotropies make cadmium a good prospect for a study of self-diffusion at high pressure. From the anisotropies of the bulk compressibilities and of the activation energies, one would hope to see an anisotropy in the activation volumes.

Another effect that can be investigated in cadmium is the temperature dependence of the activation volumes. In the absence of experimental data, a number of authors[4-6] have taken the thermal-expansion coefficient of the activation volume, α_v, to be the same as the volume thermal-expansion coefficient α_0 of the lattice. However, in the case of zinc, Gilder and Chhabildas[7,8] have found that the activation volumes are quite temperature dependent and $\alpha_v = 15\alpha_0$. By means of a model calculation,[7] they found that the temperature dependence of the activation volume is explained by the pressure dependence of the vibrational frequencies of the atoms neighboring a vacancy.

Using a thermostatically controlled, externally heated pressure cell,[9] we have measured activation volumes to a precision of about 1% and can determine if the activation-volume thermal-expansion α_v in cadmium is similar to the value found for zinc.

Our procedure has been to measure the pressure dependence of the self-diffusion rates in single crystals of cadmium along the two principal axes at four different temperatures. From this we have determined the activation volumes of self-diffusion, the anisotropy of the migration volumes, the thermal expansion of the activation volumes, the pressure dependence of the activation entropy, and the pressure dependence of the activation enthalpy.

II. THEORY

For self-diffusion by the vacancy mechanism in the hexagonal-close-packed (hcp) lattice, the activation energies of the nonbasal and basal processes are given by the expressions

$$\Delta G_c = \Delta G_f + \Delta G_m^c , \tag{1}$$

$$\Delta G_b = \Delta G_f + \Delta G_m^b , \tag{2}$$

where ΔG_c and ΔG_b are the Gibbs free energies of the nonbasal and basal mechanisms, respectively, ΔG_f is the Gibbs free energy of vacancy formation, and ΔG_m^c and ΔG_m^b are the Gibbs free energies associated with nonbasal and basal vacancy migration.

The activation volumes are the net changes in crystal volume due to a moving vacancy and are related to the activation energies by the thermodynamic relation $V = (\partial G/\partial P)_T$. The activation volumes of the two mechanisms are given by

$$\Delta V_c = \left(\frac{\partial \Delta G_c}{\partial P}\right)_T = \Delta V_f + \Delta V_m^c , \tag{3}$$

$$\Delta V_b = \left(\frac{\partial \Delta G_b}{\partial P}\right)_T = \Delta V_f + \Delta V_m^b , \tag{4}$$

where ΔV_c and ΔV_b are the activation volumes for the nonbasal and basal mechanisms, ΔV_f is the vacancy-formation volume, ΔV_m^c and ΔV_m^b are the nonbasal- and basal-vacancy-migration volumes, P is pressure, and T is the absolute temperature. The vacancy-formation volume ΔV_f is common to both activation volumes. Thus the difference in the lattice relaxation for the basal and nonbasal vacancy migration, $\Delta V_m^b - \Delta V_m^c$, is equal to the difference in the self-diffusion activation volumes, $\Delta V_b - \Delta V_c$.

In general, the activation volume for self-diffusion is temperature dependent inasmuch as it depends on the pressure dependence of both the activation entropy and the activation enthalpy. The Gibbs free energy for self-diffusion is given by the sum

$$\Delta G = \Delta H - T\Delta S , \tag{5}$$

where ΔH is the activation enthalpy, ΔS is the activation entropy, and T is the absolute temperature. The activation volume takes the form

$$\Delta V = \left(\frac{\partial \Delta H}{\partial P}\right)_T - T\left(\frac{\partial \Delta S}{\partial P}\right)_T . \tag{6}$$

From Maxwell's relations, we find

$$\left(\frac{\partial \Delta V}{\partial T}\right)_P = -\left(\frac{\partial \Delta S}{\partial P}\right)_T . \tag{7}$$

Thus the pressure dependence of the activation entropy is equal to minus the rate of change of the activation volume with temperature. And from Eqs. (6) and (7), the pressure dependence of the activation enthalpy is given by

$$\left(\frac{\partial \Delta H}{\partial P}\right)_T = \Delta V - T\left(\frac{\partial \Delta V}{\partial T}\right)_P . \tag{8}$$

According to reaction-rate theory[10] including correlation effects,[11,12] the principal-axis self-diffusion coefficients in cadmium are given by

$$D_c = \tfrac{3}{4} c^2 f_1 \nu_c e^{-\Delta G_c/RT} , \tag{9}$$

$$D_a = \tfrac{1}{2} a^2 f_2 \nu_c e^{-\Delta G_c/RT} + \tfrac{3}{2} a^3 f_3 \nu_b e^{-\Delta G_b/RT} . \tag{10}$$

The principal-axis diffusion coefficients D_c and D_a are the diffusion coefficients in the c- and a-axis directions, respectively. The lengths c and a are the lattice parameters of the hcp unit cell, ν_c and ν_b are vibration frequencies, and R is the gas constant. Inasmuch as two vacancy-jump mechanisms operate in cadmium, the correlation factors f_1, f_2, and f_3 are more than geometrical constants and depend on the ratio of the basal to nonbasal vacancy-jump frequencies.[11,12]

When diffusion coefficients are determined by serial sectioning at room temperature and pressure, it has been shown[13] that the activation volumes are given by

$$\Delta V_c = -RT \frac{\partial \ln D_c}{\partial P} + RT\kappa_c \gamma_c , \tag{11}$$

$$\Delta V_b = -RT \frac{\partial \ln (D_b)}{\partial P} + RT\kappa_a \gamma_a , \tag{12}$$

where

$$D_b = D_a - gD_c , \tag{13}$$

and κ_c and κ_a are the linear isothermal compressibilities,[14] γ_c and γ_a are the Grüneisen constants,[15] and D_b is the diffusion coefficient for the basal-plane mechanism. The factor g is the ratio

$$g = 2a_0^2 f_2 / 3c_0^2 f_1 . \tag{14}$$

Because the sectioning is performed at room temperature and pressure, the lengths c_0 and a_0 are the hcp unit-cell lattice parameters for cadmium at room temperature and pressure. The correlation factors depend on the anisotropy of the vacancy-jump rates in and out of the basal plane. For cadmium we find that any anisotropy in the pressure dependence of D_c and D_a is within our experimental uncertainty, and the correlation factors are taken to be pressure independent. The ratio f_1/f_2 for cadmium determined at zero pressure by Mao[3] is 1.012 at 227 °C and 1.005 at 315 °C, and we find that the factor g can be set equal to 0.189 over our temperature range.

III. EXPERIMENTAL PROCEDURE

A. Sample Preparation

Single crystals of cadmium were grown from 99.999%-purity cadmium purchased from Cominco American, Inc., Spokane, Wash. The crystals were grown by the Bridgman method in $\frac{3}{8}$-in.-i.d. evacuated Pyrex tubes that had been coated with Aquadag. A preliminary determination of the crystal orientation was made by an indentation technique[2] to select only those crystals with c-axis orientation within 0°–10° and 80°–90° of the cylindrical axis.

The crystals were cut into $\frac{3}{8}$-in.-long samples with an acid saw. One face of each sample was polished to a flat reflecting surface using standard techniques. The samples were then etched in a 10% nitric acid solution. This was followed by an anneal in an evacuated Pyrex capsule at 300 °C for 48 h to remove any cold work. A Laue photograph of each annealed sample was taken to determine the crystal orientation relative to the polished face. Only those samples in which the c axis made an angle of 78°–90° with the polished face (c-axis samples) and 0°–12° with the polished face (a-axis samples) were used. The tracer plated on the samples was high-specific-activity ^{109}Cd purchased from Nuclear Science and Engineering Corp., Pittsburgh, Pa.

B. Procedure

The diffusion anneals were made in a pressure vessel immersed in a thermostatically controlled molten-tin bath. The system, described in detail elsewhere,[9] made it possible to reproduce the temperature of the anneals to within ±0.1 °C. Anneals were done at nominal pressures of 0, 2, 4, 6, and 8 kbar at temperatures of 251, 276, 301, and

319 °C. For each run two samples (a c- and an a-axis sample) were wrapped in molybdenum foil with the active faces separated by a thin molybdenum disk, and the samples were placed in the pressure vessel. The vessel was pressurized and immersed in the molten tin. The run was terminated by raising the vessel from the bath and blast cooling it with a jet of compressed air. The time of the anneal t was taken to be the interval between immersion and withdrawal of the vessel. No warm-up corrections were made. The correction is small, ~ 2 min, affecting the absolute value of D by at most 2%, and, to within our experimental error, is independent of pressure.[9] Inasmuch as all of the anneals that correspond to a particular isotherm were of the same duration, warm-up corrections have no effect on the activation volume.

The isotherms were done in the sequence of 301 °C, then 251 and 276 °C concurrently, and finally 319 °C to eliminate the possibility of error in the determination of $(\partial\Delta V/\partial T)$, $(\partial\Delta S/\partial P)_T$, and $(\partial\Delta H/\partial P)_T$ arising from a drift in the calibration of the manganin cell.

The diffusion coefficients were determined by the standard lathe-sectioning technique. Each section was weighed, then dissolved in a 20% nitric acid solution, and counted in a well-type scintillation detector to at least 10^4 counts. After counting each section, a standard source and background were counted, and corrections to 1% were made for counter drift and background.

IV. RESULTS

The thin-film solution of the diffusion equation that applies to our experimental conditions has the form

$$C(x)=e^{-x^2/4Dt}\,, \tag{15}$$

where $C(x)$ is the specific activity of the sample at a distance x from the sample face, D is the diffusion coefficient normal to the face, and t is the anneal time. Penetration profiles obtained from c- and a-axis samples diffused at 251 °C at pressures of 2.04 and 8.18 kbar are shown in Fig. 1. The values of the diffusion coefficients for c- and a-axis diffusion obtained from the pressure anneals are listed in Table I.

Figures 2 and 3 show the four isotherms constructed from the data. The basal-plane diffusion coefficients are obtained from Eq. (13). In the three cases in which D_c's were not measured concurrently with the D_a's, a value for D_c was taken from the $\ln D_c$-vs-P curves.

Over our pressure range the $\ln D$-vs-P curves are found to be linear, and a least-squares fit was made to determine the slopes. Table II lists the slopes $(\partial \ln D_c/\partial P)_T$, $(\partial \ln D_b/\partial P)_T$, and the activation volumes ΔV_c, ΔV_b obtained from each isotherm.

TABLE I. Self-diffusion coefficients of cadmium.

P (kbar)	T (°C)	D_c (10^{-9} cm^2/sec)	D_a (10^{-9} cm^2/sec)
0.12	319	14.56	10.25
2.18	319	10.28	7.152
4.11	319	7.780	5.316
6.25	319	5.791	3.828
8.61	319	4.095	2.771
0.07	301	8.287	5.711
1.95	301	6.364	4.233
1.98	301	6.239	Ref. a
3.91	301	4.762	Ref. b
4.00	301	4.538	3.023
6.07	301	3.366	2.290
8.07	301	2.383	1.618
0.00	276	3.820	Ref. a
0.14	276	Ref. a	2.400
1.71	276	3.002	1.938
4.19	276	2.103	1.304
6.22	276	1.464	0.961
8.18	276	1.117	0.706
0.05	251	1.629	1.062
1.88	251	1.243	Ref. a
2.04	251	1.257	0.756
3.98	251	Ref. a	0.578
4.02	251	0.897	Ref. a
5.85	251	0.672	Ref. a
6.18	251	Ref. a	0.401
8.18	251	0.471	0.293

[a] Samples ruined during sectioning.

[b] Anneal with c-axis sample only.

Figure 4 is a plot of ΔV_c and ΔV_b versus temperature. The anisotropy of the activation volumes is small and below our experimental limits of error, as shown by

$$2\sum_i \frac{(\Delta V_c-\Delta V_b)_i}{(\Delta V_c+\Delta V_b)_i}=0.3\pm 1.3\%\,. \tag{16}$$

The temperature dependence of the activation volumes is found by assuming they are isotropic. By applying a least-squares fit to the expression

$$\Delta V=\Delta V_0+T\left(\frac{\partial\Delta V}{\partial T}\right)_P\,, \tag{17}$$

we find $\Delta V_0=1.1\pm 0.8$ cm^3/mole and $(\partial\Delta V/\partial T)_P=0.011\pm 0.002$ cm^3/mole °K. Using Eqs. (6) and (7), the pressure dependences of the activation enthalpy and entropy are, respectively, $(\partial\Delta H/\partial P)_T=1.1\pm 0.8$ cm^3/mole and $(\partial\Delta S/\partial P)_T=-0.011\pm 0.002$ cm^3/mole °K.

The data can also be presented in the form of isobars, as in Figs. 5 and 6. In these the diffusion coefficients are normalized to 0, 2, 4, 6, and 8 kbar by a simple correction. The values of ΔH and $\ln D_0$ obtained from the isobars are listed in Table III and plotted versus pressure in Figs. 7 and 8. Least-squares-fit lines to the $\ln D_0$-vs-P curves

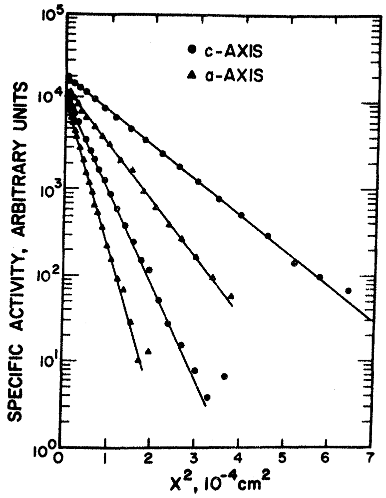

FIG. 1. Penetration profiles of self-diffusion in cadmium at 251 °C. The two upper curves are from a 2.04-kbar anneal, and the two lower curves are from an 8.18-kbar anneal.

give the slopes $(\partial \ln D_{0c}/\partial P)_T = -0.13 \pm 0.03$ kbar^{-1} and $(\partial \ln D_{0b}/\partial P)_T = -0.11 \pm 0.04$ kbar^{-1} and the associated pressure derivatives of the activation entropies $(\partial \Delta S_c/\partial P)_T = -0.012 \pm 0.002$ cm^3/mole °K and $(\partial \Delta S_b/\partial P)_T = -0.009 \pm 0.003$ cm^3/mole °K. Least-squares-fit lines to the ΔH-vs-P curves give the slopes $(\partial \Delta H_c/\partial P)_T = 0.02 \pm 0.03$ kcal/kbar or 0.8 ± 1.2 cm^3/mole and $(\partial \Delta H_b/\partial P)_T = 0.06 \pm 0.05$ kcal/kbar or 2.5 ± 2.1 cm^3/mole. These are consistent with the average values of $(\partial \Delta S/\partial P)_T$ and $(\partial \Delta H/\partial P)_T$ obtained from the temperature dependence of the activation volumes.

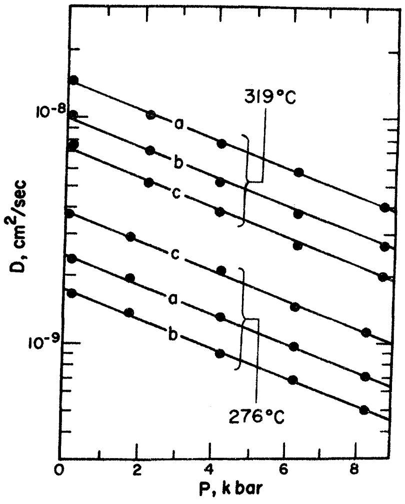

FIG. 2. Isotherms of $\ln D_c$, $\ln D_a$, and $\ln D_b$ vs P for the temperatures 319 and 276 °C.

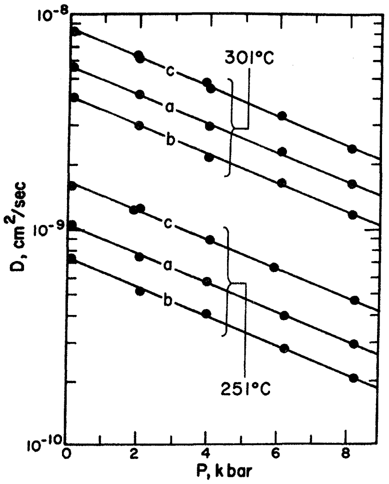

FIG. 3. Isotherms of $\ln D_c$, $\ln D_a$, and $\ln D_b$ vs P for the temperatures 301 and 251 °C.

V. DISCUSSION

A. Anisotropy

Although there appears to be a systematic difference in the slopes of the $\ln D$-vs-P curves for the two diffusion mechanisms, when the $\kappa\gamma$ terms are added, the activation volumes ΔV_c and ΔV_b are found to be equal to within the precision of our measurements. Similar results have been found for two other hcp metals, zinc[7,8,16] and beryllium,[17] in which no significant anisotropy in the activation volumes was found. The upper limit we find for the the anisotropy is $|\Delta V_c - \Delta V_b| \lesssim 0.1$ cm^3/mole. Although the possible anisotropy is quite small in terms of the total activation volumes, ~1.5%, it could correspond to about a 10% difference in the migration volumes of the two mechanisms. Inasmuch as good reasons exist to expect that $\Delta V_f \approx 4\Delta V_m$,[17] the migration volume may only contribute to about 20% of the self-diffusion activation volume. In this case, a 10% anisotropy in the mi-

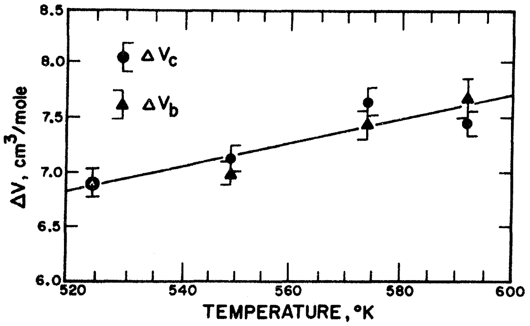

FIG. 4. Temperature dependence of the activation volumes in cadmium.

TABLE II. Isotherm slopes and activation volumes for cadmium.

T (°C)	$-[\partial \ln D_c/\partial P]_T$ (kbar^{-1})	$-[\partial \ln(D_a - gD_c)/\partial P]_T$ (kbar^{-1})	ΔV_c (cm^3/mole)	ΔV_b (cm^3/mole)
251	0.154 ± 0.003	0.158 ± 0.003	6.90 ± 0.13	6.91 ± 0.13
276	0.152 ± 0.003	0.153 ± 0.002	7.14 ± 0.14	7.01 ± 0.09
301	0.156 ± 0.002	0.156 ± 0.003	7.65 ± 0.10	7.47 ± 0.14
319	0.148 ± 0.003	0.156 ± 0.004	7.49 ± 0.15	7.71 ± 0.20

gration volumes would only result in a 2% anisotropy in the total activation volumes, which is of the order of the experimental limit of error of the present work.

B. Temperature Dependence of Activation Volumes

The activation volumes in cadmium are found to be temperature dependent between 524 and 592 °K. Over this temperature range the activation volumes for both c-axis and basal-plane diffusion are given by

$$\Delta V = [1.1 \pm 0.8 + (0.011 \pm 0.002)T] \text{ cm}^3/\text{mole}. \tag{18}$$

In this expression, the first term, 1.1 ± 0.8 cm^3/mole, is from the pressure dependence of the activation enthalpy; the second term, $(0.011 \pm 0.002)T$, comes from the pressure dependence of the activation entropy. Thus, in the temperature range of our diffusion experiments, we find that $-T(\partial \Delta S/\partial P)_T$ makes the largest contribution to the activation volume in cadmium and that the activation volume is almost proportional to the absolute temperature.

The thermal-expansion coefficient of the activated state in cadmium,

$$\alpha_V = \left(\frac{1}{\Delta V}\right)\left(\frac{\partial \Delta V}{\partial T}\right), \tag{19}$$

has the value (0.0015 ± 0.003)°C^{-1} between 250 and 319 °C. This is more than an order of magnitude larger than the lattice thermal-expansion coefficient of cadmium at 250 °C, $\alpha_0 = 0.00012$ °C^{-1}.[18]

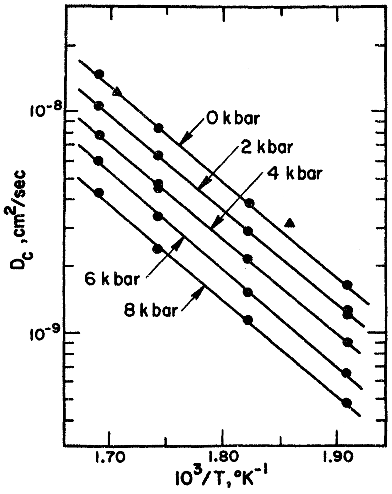

FIG. 5. Isobars of $\ln D_c$ vs $1/T$ at pressures of 0, 2, 4, 6, and 8 kbar. The solid triangles are data from Ref. 3.

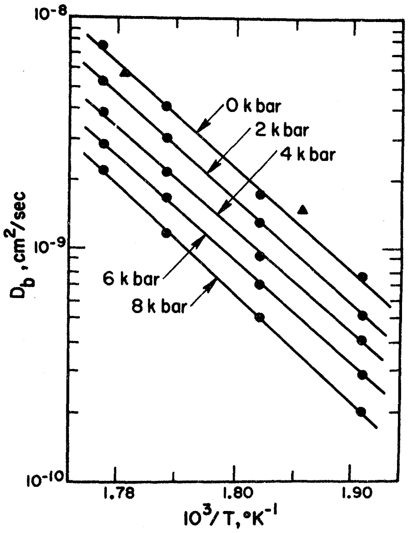

FIG. 6. Isobars of $\ln D_b$ vs $1/T$ at pressures of 0, 2, 4, 6, and 8 kbar. The solid triangles are data from Ref. 3.

These results are similar to the results found in a study of diffusion in zinc by Chhabildas and Gilder.[8] In zinc the largest contribution to the activation volume was also found to come from the entropy term $T(\partial \Delta S/\partial P)_T$, and the thermal-expansion coefficient of the activated state was also found to be large compared to the lattice thermal expansion, $\alpha_v \cong 15\alpha_0$.

C. Pressure Dependence of Activation Volume

The activation energy ΔG can be expanded in a Taylor series in pressure by

$$\Delta G = \Delta G(0) + \left(\frac{\partial \Delta G}{\partial P}\right)_T P + \frac{1}{2}\left(\frac{\partial^2 \Delta G}{\partial P^2}\right)_T P^2 , \tag{20}$$

$$\Delta G = \Delta G(0) + \Delta V_0 P + \tfrac{1}{2}\kappa_v \Delta V_0 P^2 , \tag{21}$$

where ΔV_0 is the activation volume at zero pressure and κ_V is the isothermal compressibility of the activated state. From Eqs. (9), (10), and (21), we find that the pressure dependence of $RT \ln D$ takes the form

TABLE III. Activation enthalpies and preexponential factors of cadmium.

P (kbar)	ΔH_c (kcal/mole)	ΔH_b (kcal/mole)	$\ln D_{0c}$	$\ln D_{0b}$
0	19.87 ± 0.19	21.00 ± 0.48	−1.14 ± 0.17	−0.85 ± 0.43
2	19.40 ± 0.12	21.08 ± 0.11	−1.87 ± 0.11	−1.12 ± 0.05
4	19.61 ± 0.16	20.52 ± 0.36	−1.98 ± 0.14	−1.93 ± 0.32
6	20.03 ± 0.24	20.87 ± 0.13	−1.92 ± 0.22	−1.92 ± 0.12
8	19.78 ± 0.34	21.69 ± 0.18	−2.45 ± 0.31	−1.51 ± 0.17

$$RT\ln D = A - (\Delta V_0 - RT\kappa\gamma)P - \tfrac{1}{2}\kappa_v \Delta V_0 P^2\,, \qquad (22)$$

where A is a constant and $\kappa\gamma$ is an appropriate frequency-factor correction. From a least-squares fit of this expression to our isotherm, we find to within our experimental uncertainty that the activation volumes in cadmium are independent of pressure and can only get an upper limit for the compressibility $\kappa_v \lesssim 0.006$ kbar^{-1}. This is about two or three times the volume compressibility of cadmium, $\kappa_0 = 0.0023$ kbar^{-1}, in contrast to the ratio found for the coefficients of thermal expansion $\alpha_v/\alpha_0 \simeq 12$. This result does not agree with the calculations of Girifalco[19] and Girifalco and Welch,[20] whose studies indicate that $\alpha_v/\alpha_0 = \kappa_v/\kappa_0$.

D. Pressure Dependence and Zero-Pressure Intercepts of Activation Enthalpy and Preexponential Factor

By analyzing our diffusion coefficients in the form of isobars, a direct comparison can be made to previous work at zero pressure. At constant pressure, along an isobar, the diffusion coefficients are given by

$$D = D_0 e^{-\Delta H/RT}\,, \qquad (23)$$

where the D_0's and the ΔH's are constants at a fixed pressure.

From the curves generated from the $\ln D$-vs-$1/T$ plots shown in Figs. 5 and 6, the preexponential factor D_0 and the activation enthalpy ΔH are found for each isobar. Inasmuch as the diffusion anneals were only made at four temperatures, the errors in determining the D_0's and the ΔH's obtained from the mean-square deviation of the experimental points from the least-square-fit curves must be taken only as a general indication of random error. In Figs. 7 and 8 one sees that the scatter is considerable in the D_0's and ΔH's. However, the trend is definite for $\ln D_0$ to decrease with increasing pressure. If the diffusion coefficient is expressed in the form

$$D(T, P) = D(0)\exp\left(\frac{(\partial\Delta S/\partial P)P}{R} - \frac{\Delta H_0 - (\partial\Delta H/\partial P)P}{RT}\right), \qquad (24)$$

we find that the diffusion coefficients in cadmium are given by

$$D_c(T, P) = (0.26 \pm 0.04)\, e^{(-0.12\pm 0.02)P} \times \exp\{[(19.7 \pm 0.2) + (0.02 \pm 0.03)P]/RT\}\ \text{cm}^2/\text{sec} \qquad (25)$$

and

$$D_b(T, P) = (0.35 \pm 0.07)\, e^{(-0.13\pm 0.03)P} \times \exp\{[(20.8 \pm 0.2) + (0.06 \pm 0.04)P]/RT\}\ \text{cm}^2/\text{sec}\,, \qquad (26)$$

where R is in kcal/mole and P is the kbar.

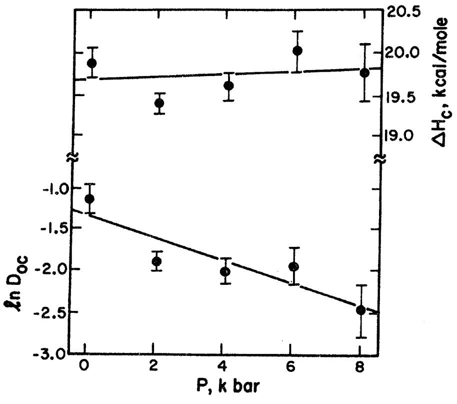

FIG. 7. Pressure variation of ΔH_c and $\ln D_{0c}$.

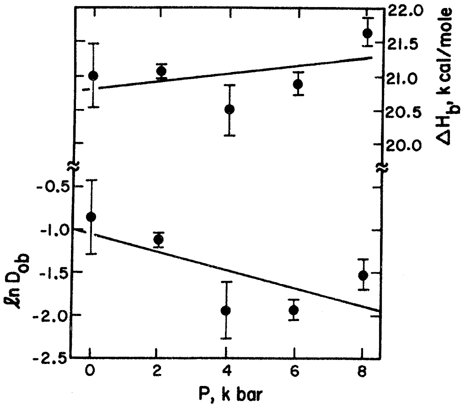

FIG. 8. Pressure variation of ΔH_b and $\ln D_{0b}$.

These results are in fair agreement with the Wadja–Shirn–Huntington (Ref. 2) and Mao (Ref. 3) zero-pressure measurements. For self-diffusion in cadmium, Wadja, Shirn, and Huntington found $D_c = 0.05$ cm^2/sec, $Q_c = 18.2$ kcal/mole, $D_b = 0.09$ cm^2/sec, and $Q_b = 19.4$ kcal/mole, whereas the measurements of Mao gave $D_c = 0.11$ cm^2/sec, $Q_c = 18.6$ kcal/mole, $D_b = 0.16$ cm^2/sec, and $Q_b = 19.9$ kcal/mole. The fact that our results are only in fair agreement with the zero-pressure results is due to our limited temperature range. Wadja, Shirn, and Huntington made diffusion anneals over the range 127–310 °C, and Mao performed anneals between 137 and 313 °C, whereas our anneals were between 251 and 319 °C. Our limited temperature range has two effects on our determination of the preexponential factors and activation enthalpies. The first, and most obvious, is that the range of $1/T$ in our $\ln D$-vs-$1/T$ curves is small and only goes from (1.90×10^{-3}) to $(1.69\times 10^{-3})\,^\circ\text{K}^{-1}$, while the zero-pressure diffusion coefficients were found over $1/T$ intervals of (3.33×10^{-3}) to $(1.83\times 10^{-3})\,^\circ\text{K}^{-1}$ and (3.22×10^{-3}) to $(1.71\times 10^{-3})\,^\circ\text{K}^{-1}$. Consequently, our results are quite sensitive to small errors in temperature determination.

The second effect is that the activation energies and entropies of self-diffusion in cadmium increase with temperature, and the average values of ΔS and ΔH over our temperature range are higher than the average values of ΔS and ΔH over the temperature ranges of the zero-pressure determinations. An increase in ΔS and ΔH with temperature is predicted from the temperature dependence of the activation volume. In Sec. V F, a calculation is made which shows that the agreement of our results with the zero-pressure results is within the experimental uncertainties.

E. Calculation of Variation of Vacancy Formation Entropy with Pressure

Gilder and Chhabildas have made a model calculation of the pressure variation of the formation entropy of a vacancy in zinc. The calculation was made using the high-temperature approximation of the Einstein model for the frequencies of lattice vibration. For zinc they also assumed an ideal hcp structure, and for the interatomic potential, a direction-independent two-body interaction patterned after the Morse potential. The expression obtained for the pressure dependence of the formation entropy is

$$\left(\frac{\partial \Delta S_f}{\partial P}\right)_T = \tfrac{1}{3} R r_0 (2\kappa_a + \kappa_c)\alpha^3 \delta_1^2 \times \left[545 + 36\sqrt{2}\,\alpha\delta_1\left(\frac{\delta_2}{\delta_1}\right) + 270\left(\frac{\delta_2}{\delta_1}\right)^2 - \frac{30}{\alpha\delta_1}\right], \tag{27}$$

where r_0 is the equilibrium interatomic separation, κ_a and κ_c are the linear compressibilities in the c- and a-axis directions, respectively, α^{-1} is the range parameter, and δ_1 and δ_2 are the first- and second-nearest-neighbor displacements.

For cadmium we set $r_0 = 2.97$ Å and $\alpha = 1.18$ Å^{-1} and varied δ_1 from $3\times 10^{-2} r_0$ to $8\times 10^{-2} r_0$. The term δ_2/δ_1 was varied from 0 to 0.5.

With these parameters, the expression of Gilder and Chhabildas gives

$$0.0006 < \left(\frac{\partial \Delta S_f}{\partial P}\right)_T < 0.009 \ \frac{\text{cm}^3}{\text{mole}\,^\circ\text{K}}, \tag{28}$$

which compares reasonably well with our observed value of $(\partial \Delta S/\partial P)_T = 0.011$ cm^3/mole °K for cadmium, considering the approximations made in the calculation.

The model predicts that the vacancy-formation volume is temperature dependent in materials for which a Morse-type potential is a realistic model of the true interatomic potential. Thus for the close-packed metals it is likely that the activation volume is generally temperature dependent. This raises some doubt about the validity of comparing the activation volume of self-diffusion to the sum of the formation volume and the motional volume determined from quenching experiments, because the self-diffusion activation volume,[21] the formation volume,[22,23] and the motional volume[24,25] are not generally determined at the same temperature.

F. Temperature Dependence of Activation Enthalpy

The variation of the activation enthalpy with temperature for the vacancy mechanism has been estimated by Nowick and Dienes,[4] Levinson and Nabarro,[5] and Girifalco.[6] Each of these authors has taken $\alpha_v/\alpha_0 \sim 1$ and found that the activation enthalpy will only vary by about 2% over the range of temperatures typical of diffusion measurements.

The ratio $\alpha_v/\alpha_0 = 12$ found for cadmium results in a much larger variation of the activation enthalpy with temperature. Following the treatment of Levinson and Nabarro, we find

$$\left(\frac{\partial \Delta S}{\partial T}\right)_P = \left(\frac{\alpha_0^2}{\kappa_0}\right)\Delta V\left(\frac{2\alpha_v}{\alpha_0} - \frac{\kappa_v}{\kappa_0}\right). \tag{29}$$

From the possible curvature of the isotherms of cadmium, we find the ratio κ_v/κ_0 is of the order of unity and can be neglected in view of the size and the error limits of the term $2\alpha_v/\alpha_0$. Thus we can write

$$\left(\frac{\partial \Delta S}{\partial T}\right)_P = \left(\frac{2\alpha_0}{\kappa_0}\right)\left(\frac{\partial \Delta V}{\partial T}\right)_P. \tag{30}$$

The activation entropy and enthalpy can be expanded about an arbitrary temperature T_0 by the expressions

$$\Delta S(T) = S(T_0) + \left(\frac{2\alpha_0}{\kappa_0}\right)\left(\frac{\partial \Delta V}{\partial T}\right)_P (T - T_0) \tag{31}$$

and

$$\Delta H(T) = H(T_0) + \left(\frac{\alpha_0}{\kappa_0}\right)\left(\frac{\partial \Delta V}{\partial T}\right)_P (T^2 - T_0^2) \tag{32}$$

using the relation

$$\left(\frac{\partial \Delta H}{\partial T}\right)_P = T\left(\frac{\partial \Delta S}{\partial T}\right)_P. \tag{33}$$

Equations (31) and (32) predict that the activation enthalpies and the preexponential factors found in the study should be larger than those seen in the zero-pressure studies. If we let $T_0 = 500$ °K, the approximate midpoint of the temperature range of the zero-pressure work, and $T = 560$ °K, the midpoint of our temperature range, we find $\Delta H(560\,^\circ\text{K}) - \Delta H(500\,^\circ\text{K}) = 0.9$ kcal/mole and $D_0(560\,^\circ\text{K})/D_0(500\,^\circ\text{K}) = 5$. This is in general agreement with what is found experimentally, namely, that the observed increase in the activation enthalpy is about 1.2 kcal/mole, and the ratios of the preexponential factors fall in the range 2–5.

The temperature-dependent enthalpies and entropies in cadmium give rise to curved Arrhenius plots for the self-diffusion coefficients. At zero pressure, the diffusion coefficients D_c and D_b take the form

$$D(T) = nfa^2\nu\, e^{\Delta S(T)/R - \Delta H(T)/RT} , \tag{34}$$

and using Eq. (31) and (32),

$$D(T) = nfa^2\nu \exp\left(\frac{\Delta S(T_0)}{R} - \frac{\Delta H(T_0)}{RT}\right) \times \exp\left[\frac{\alpha_0}{\kappa_0}\left(\frac{\partial \Delta V}{\partial T}\right)_P \frac{(T-T_0)^2}{RT}\right] . \tag{35}$$

Over the temperature range of self-diffusion studies in cadmium, i.e., 125–320 °C,

$$\left(\frac{\alpha_0}{\kappa_0}\right)\left(\frac{\partial \Delta V}{\partial T}\right)_P \frac{(T-T_0)^2}{RT} \ll 1$$

when T_0 is set at the midpoint, and Eq. (35) is approximated by

$$D(T) = nfa^2\nu \exp\left(\frac{\Delta S(T_0)}{R} - \frac{\Delta H(T_0)}{RT}\right) \times\left[1 + \left(\frac{\alpha_0}{\kappa_0}\right)\left(\frac{\partial \Delta V}{\partial T}\right)_P \frac{(T-T_0)^2}{RT}\right] . \tag{36}$$

Wadja, Shirn, and Huntington investigated self-diffusion in cadmium between 400 and 583 °K. If we take T_0 to be 490 °K at $T = 583$ °K,

$$\left(\frac{\alpha_0}{\kappa_0}\right)\left(\frac{\partial \Delta V}{\partial T}\right)_P \frac{(T-T_0)^2}{RT} = 0.10 .$$

At $T = 400$, a similar result is found. Thus the curvature in the Arrhenius plot is barely noticeable since the deviation of the diffusion coefficients to a least-squares-fit straight line of ln$D$ vs $1/T$ is at most about 5%.

VI. SUMMARY

The effect of pressure on the self-diffusion rates in cadmium along the principal axes has been investigated. The activation volumes for the two vacancy mechanisms in cadmium were found to be temperature dependent, isotropic to within 1.6%, and of the form

$$\Delta V = 1.1 \pm 0.8 + (0.011 \pm 0.002) T(°\mathrm{K})\ \mathrm{cm}^3/\mathrm{mole}.$$

The activation enthalpy was found to be independent of pressure within our experimental uncertainty,

$$\left(\frac{\partial \Delta H}{\partial P}\right)_T = 1.1 \pm 0.8\ \frac{\mathrm{cm}^3}{\mathrm{mole}} ,$$

and the activation entropy was found to be pressure dependent,

$$\left(\frac{\partial \Delta S}{\partial P}\right)_T = -0.011 \pm 0.002\ \frac{\mathrm{cm}^3}{\mathrm{mole}\,°\mathrm{K}} .$$

The activation entropies and the preexponential factors for diffusion at zero pressure observed in this investigation are higher than those found by previous measurements by an amount consistent with the increase in ΔH and D_0 calculated from the expression

$$\left(\frac{\partial \Delta S}{\partial T}\right)_P = \left(\frac{2\alpha_v}{\kappa_v}\right)\left(\frac{\partial \Delta V}{\partial T}\right)_P .$$

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