PHYSICAL REVIEW B VOLUME 15, NUMBER 12 15 JUNE 1977

Diffusion of mercury and cadmium in lead at high pressures*

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(Received 11 March 1977)

The diffusion of Hg and Cd in solid lead has been measured at hydrostatic pressures to 40 kbar for temperatures between 250 and 550°C using the radiotracer sectioning technique. The data were analyzed assuming a single effective mechanism of diffusion with a temperature- and pressure-dependent activation volume. The activation energy and activation volume at zero pressure and 600 K are, respectively, $\Delta H = 23.10 \pm 0.14$ kcal/mole, $\Delta V/V_0 = 0.516 \pm 0.006$ for Hg in Pb: $\Delta H = 22.17 \pm 0.18$ kcal/mole, $\Delta V/V_0 = 0.317 \pm 0.010$ for Cd in Pb. The pressure and temperature coefficients of the activation volume along with the specific heat of activation, although quite uncertain are also determined. Even though the activation energies for the diffusion of both Hg and Cd in Pb is near that for lead self-diffusion, the activation volume is too small in both cases to be consistent with a vacancy mechanism.

I. INTRODUCTION

The diffusion of Hg and Cd into Pb was reported to be a factor of 10 and 20, respectively, times that of Pb self-diffusion by Seith *et al.*, in the 1930's.[1] However, much of the early work on diffusion of metals in lead focused on the faster diffusers such as Au and Ag, which were observed to diffuse three or four orders of magnitude faster than Pb self-diffusion.[2] Early enhancement measurements led Seith and Keil to conclude that Au and Ag diffuse in Pb by an interstitial mechanism.[3] This view was accepted for at least thirty years.[4]

In recent years, however, more definitive experiments such as linear enhancement,[4-7] isotope effects,[8,9] high-pressure measurements,[10-14] internal friction,[15,16] and effective-charge measurements[17,18] have demonstrated that a simple interstitial mechanism cannot explain the observed results for rapid diffusers in Pb. At the same time, renewed interest in the slower diffusers in Pb, such as Cd and Hg, led to experiments which indicated that the diffusion of these metals does not obey a simple substitutional mechanism as had been assumed previously. As a result of linear enhancement,[19] and isotope effect,[20] measurements for Cd in Pb, Miller[21] proposed a dissociative model involving substitutional, interstitial, and interstitial-vacancy pair defects. Subsequently, Warburton[22] demonstrated that a model allowing these three types of defects was consistent with his linear dehancement measurements for Hg in Pb.[23]

High-pressure diffusion measurements shed further light on this complex picture by supplying the activation volume. In this laboratory, activation volumes have been measured for Ag,[10] Au,[11] Cu,[12] Ni,[13] Pd,[14] and Zn,[24] in Pb. These measurements confirm the fact that diffusion of these metals in Pb cannot be explained using a single simple interstitial or substitutional mechanism. Decker *et al.*[14] point out that at least three defects are required to construct a suitable model for these various impurities in Pb.

The activation volumes for Hg in Pb and Cd in Pb reported here are especially interesting quantities because Hg and Cd represent the slowest impurity diffusers in Pb for which an activation volume has yet been measured. Knowledge of the activation volume is particularly meaningful for the slower diffusers since a substitutional model requires an activation volume large enough to account for vacancy formation.

II. EXPERIMENTAL PROCEDURE

Diffusion rates were measured by the radioactive tracer and sectioning technique. A total of 32 diffusion measurements were made along isobars at 1 bar, 10.5, 17.6, 25.4, 32.1, and 38.3 kbar for Hg in Pb and 26 measurements along isobars at 1 bar, 18.1, 25.1, 31.8, 35.7, and 40.3 kbar for Cd in Pb.

Single-crystal-lead samples, 99.9999% pure, in the form of right circular cylinders 0.32 cm long by 0.32 cm diam were electroplated on one end surface with either mercury 203 from a 0.5*N* nitric acid solution or cadmium 109 from a 10.5*p*H sodium cyanide solution. A chromel-alumel thermocouple junction was embedded in the opposite end surface and the thermocouple leads were used to suspend the sample in a thin-walled inconel tube 2.5 cm long and 0.64 cm diam positioned along the main diagonal of a 2.46-cm pyrophyllite cube. The metal tube serves as an internal heater. The ends of the tube were sealed with polyethylene plugs and petroleum ether was used as the hydrostatic liquid.[24]

Each sample was first brought to the desired pressure in a 400-ton hexahedral anvil press and then annealed at the desired temperature. Anneal times were selected to give concentration profiles dropping three orders of magnitude in a few hundred microns.

The high-pressure cell was calibrated by observing room-temperature phase transitions in mercury, bismuth, and thallium. The correction to sample pressure due to heating was measured by observing bismuth transitions at elevated temperatures. The problem of press calibration at elevated temperatures has been discussed in detail by Decker, Jorgensen, and Young.[25]

After the diffusion anneals, the lead samples were sectioned into 10-μm slices using a sliding-blade microtome. The mercury 203 or cadmium 109 concentration was measured in each slice with a scintillation counter.

III. METHOD OF ANALYSIS

The analysis of diffusion measurements as a function of temperature and pressure is generally reported in terms of a single effective mechanism of diffusion. This approach can be justified for a multiple-diffusion mechanism if the contributing defect concentrations are in thermal equilibrium at all times. It must be realized, however, that the measured or effective diffusivities, activation energies, and activation volumes must be interpreted in terms of the analogous quantities of the proposed multiple-mechanism model.

For a single mechanism, the measured or effective diffusion coefficient based on kinetic theory and equilibrium thermodynamics can be written[11]

$$D(P,T)=fa^2\nu(P,T)e^{-\Delta G(P,T)/kT}, \qquad (1)$$

where f is the so-called correlation factor and a is the lattice parameter (a constant for our experiment since all samples were sectioned at atmospheric pressure and room temperature).[26] The quantity ν is a characteristic vibrational frequency of the diffusing atoms, ΔG is the Gibbs free energy of activation of activated complexes, k is Boltzmann's constant, P is the pressure, and T is the absolute temperature. Following the analysis of Weyland *et al.*,[11] $\ln\nu(P,T)$ and $\Delta G(P,T)$ were expanded in Taylor series through second order around $P=0$ and $T=T_0=600$ K (Pb melting point at zero pressure) to give the expression

$$D(P,T)=D_0(P,T)e^{-\Delta H(P,T)/kT}, \qquad (2)$$

where

$$\begin{aligned}\ln D_0(P,T)=\ln D_0(0,T_0)&-\gamma(T-T_0)\left(\beta+\tfrac{1}{2}(T-T_0)\frac{\partial\beta}{\partial T}\right)\\&+\gamma P\left(\kappa+(T-T_0)\frac{\partial\kappa}{\partial T}+\tfrac{1}{2}P\frac{\partial\kappa}{\partial P}\right)\\&-\frac{P}{k}\left(\frac{\partial\Delta V}{\partial T}\right)_P+(T-T_0)\frac{\Delta C_P}{kT_0}\end{aligned} \qquad (3)$$

and

$$\begin{aligned}\Delta H(P,T)=\Delta H(0,T_0)+P\Delta V(0,T_0)&+\frac{P^2}{2}\left(\frac{\partial\Delta V}{\partial P}\right)_T\\&-PT_0\left(\frac{\partial\Delta V}{\partial T}\right)_P+\tfrac{1}{2}(T^2-T_0^2)\frac{\Delta C_P}{T_0},\end{aligned} \qquad (4)$$

$$\Delta C_p=\Delta C_v+\frac{\beta^2T_0}{\kappa}\left[\frac{2}{\beta}\left(\frac{\partial\Delta V}{\partial T}\right)_P+\frac{1}{\kappa}\left(\frac{\partial\Delta V}{\partial P}\right)_T\right]. \qquad (5)$$

The partial derivatives are all evaluated at $P=0$ and $T=T_0$; γ is the Grüneisen constant, β is the volume coefficient of thermal expansion, and κ is the isothermal compressibility.

The preexponential factor $D_0(0,T_0)$, the activation energy or enthalpy $\Delta H(0,T_0)$, the activation volume $\Delta V(0,T_0)$, and the pressure and temperature derivatives of the activation volume were determined by a least-squares fit of Eq. (2) to all of the diffusion data simultaneously. The specific heat of activation ΔC_p was evaluated as shown in Eq. (5) following the derivation of Gilder and Lazarus[27] with the approximation that ΔC_v is small and can be neglected.

IV. RESULTS

Typical concentration profiles are shown in Figs. 1 and 2 for diffusion of Hg and Cd in Pb, respectively. Measurements were made for pressures of up to 40 kbar over the temperature range 250–550°C and with anneal times between 1 and 140 h.

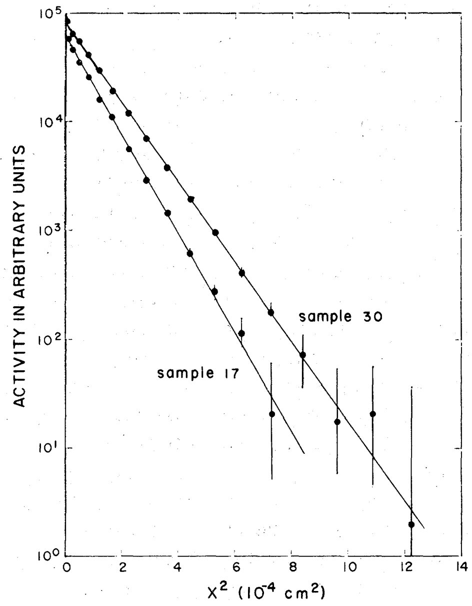

FIG. 1. Concentration profiles for the diffusion of Hg in Pb. Sample 17 was annealed for 183 min at 10.5 kbar and 360.8 °C, and sample 30 was annealed for 100 min at 38.2 kbar and 541.7 °C.

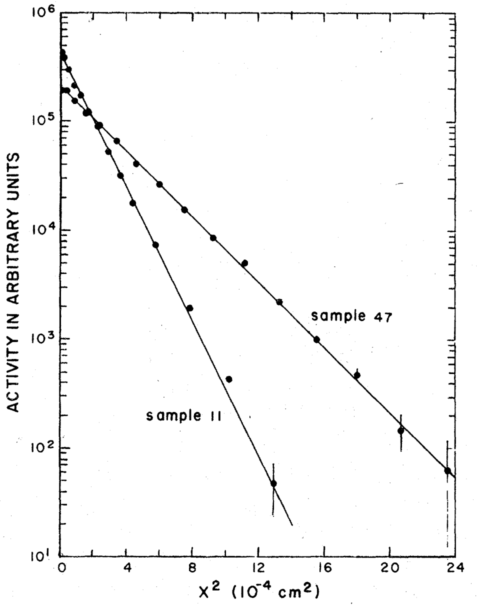

FIG. 2. Concentration profiles for the diffusion of Cd in Pb. Sample 11 was annealed for 642 min at 1 bar and 260 °C, and sample 47 was annealed for 295.7 min at 36.9 kbar and 501 °C.

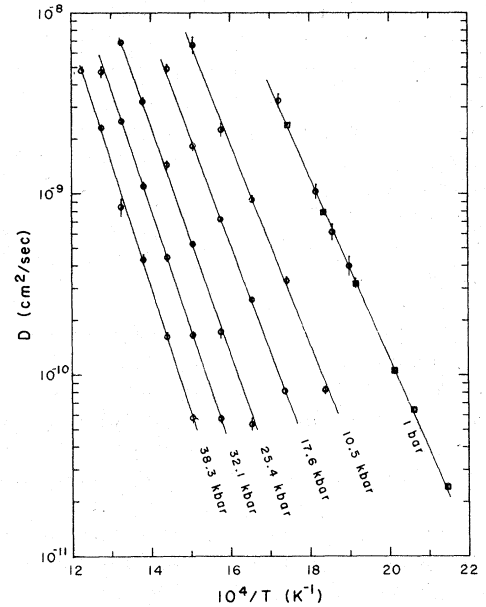

FIG. 3. Variation of diffusivity with inverse temperature for Hg in Pb along selected isobars. Atmospheric pressure points from Ref. 23, shown as squares, are included for comparison.

It should be noted that all of the penetration profiles were very nearly Gaussian in shape. Also, one additional advantage in making diffusion measurements at high pressure is the increased temperature range, i.e., the melting temperature increases from 327 °C at 1 bar to 603 °C at 40 kbar.

The measured diffusion coefficients for Hg in Pb as a function of reciprocal temperature are shown in Fig. 3 for several isobars. Also shown for comparison are the atmospheric-pressure measurements of Warburton.[23] The measured diffusion coefficients along various isobars for Cd in Pb as a function of reciprocal temperature are likewise shown in Fig. 4. Also shown for comparison are the atmospheric-pressure measurements of Miller.[19] Precise pressure settings are difficult to attain primarily because of the cell-pressure correction due to heating (1.6 kbar/100 °C), and secondly because of small drifts in the hydraulic load with time. Therefore, the data shown in Figs. 3 and 4 have been corrected to isobars using Eq. (2). The corrections amounted to less than 1.5 kbar in all cases.

The larger uncertainties for the atmospheric-pressure data were the result of using a less-sophisticated temperature-control system as compared to that used for the high-pressure runs. The uncertainty assigned to each diffusion coefficient includes contributions from the statistical uncertainty of the concentration profile, an estimated pressure uncertainty of ±4%, and a temperature uncertainty of ±2 °C or ±0.75% of the thermocouple voltage (whichever is greater). For a few particular runs additional contributions to the uncertainty resulted from observed variations in the temperature or pressure during the anneal.

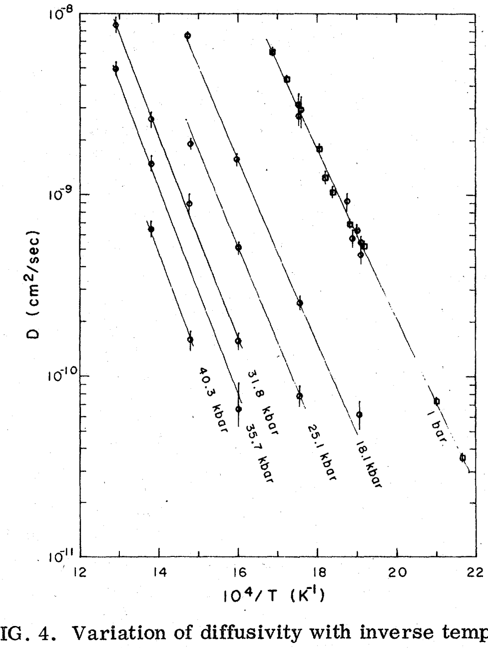

FIG. 4. Variation of diffusivity with inverse temperature for Cd in Pb along selected isobars. Atmospheric pressure points from Ref. 19, shown as squares, are included for comparison.

TABLE I. Parameters for impurity diffusion of Hg and Cd into Pb evaluated at zero pressure and $T_0 = 600$ K. At the reference temperature and pressure $V_0 = 18.796$ cm^3/mole.

Impurity	$D_0(0,T_0)$ (cm^2/sec)	$\Delta H(0,T_0)$ (kcal/mole)	$\frac{\Delta V(0,T_0)}{V_0}$	$\frac{1}{V_0}\left(\frac{\partial \Delta V}{\partial P}\right)_T$ (10^{-3} kbar^{-1})	$\frac{1}{V_0}\left(\frac{\partial \Delta V}{\partial T}\right)_P$ (10^{-4} K^{-1})	$\frac{\Delta C_p(0,T_0)}{R}$
Hg	1.50 ± 0.20	23.10 ± 0.14	0.516 ± 0.006	-0.4 ± 0.3	0.3 ± 0.3	0.2 ± 0.3
Cd	0.92 ± 0.15	22.17 ± 0.18	0.317 ± 0.010	$+5.5 \pm 0.7$	3.7 ± 0.6	4.6 ± 0.5

Table I shows the experimental values for the preexponential factor D_0, the activation energy ΔH, the activation volume $\Delta V/V_0$, and the pressure and temperature derivatives of the activation volume, all evaluated at zero pressure and 600 K for Hg and Cd in Pb. These five parameters were obtained from a least-squares fit of all the experimental data to Eq. (2). The pressure dependence of the activation energy for Hg, as determined from Eq. (4), is very nearly linear since the activation volume is essentially constant within the limits of the experimental uncertainty. However for Cd the activation volume is very pressure dependent.

V. DISCUSSION

The vacancy mechanism has been shown to be the mechanism responsible for self-diffusion in fcc metals by several different types of experiments.[28,29] There has been limited success, however, in explaining impurity diffusion in Pb in terms of a vacancy mechanism. For vacancy diffusion, the activation energy and activation volume must each include a term for the formation of the vacancy. The energy of formation for vacancies in Pb has been reported to be 12.0 kcal/mole by one group[30] and 13.3 kcal/mole by another,[31] and the energy of motion has been reported to be 14.8 kcal/mole.[32] The corresponding volumes of formation and motion for vacancies in Pb have not been measured, but values have been reported for vacancies in Au. The volume of vacancy formation has been reported as 0.55 atomic volumes,[33] and the volume of motion as 0.15 atomic volumes.[34] These numbers are very consistent with the activation volume for self-diffusion in Au which has been reported as 0.71 atomic volumes.[35] The activation volume for self-diffusion in Pb has been reported by different workers as 11.6 (at 325 °C),[36] 13.0 ± 0.8 (at 301 °C),[37] and 13.30 ± 0.32 (at 265, 295, and 325 °C)[38] cm^3/mole. The data of Ref. 36 was corrected using the currently accepted pressure calibration scale and found to have a value of 13.2 (at 327 °C) cm^3/mole. The most reliable measurement, Ref. 38, gives an activation volume of 0.71 ± 0.02 atomic volumes. Since Au and Pb are both fcc metals with very similar activation volumes for self-diffusion, one is tempted to assume that the volume of vacancy formation in Pb is also about 0.55 atomic volumes.

It is clear that for both Hg and Cd in Pb the activation energy is consistent with a vacancy mechanism, but the activation volume is too small for such a mechanism in both cases. This conclusion, that neither Hg or Cd in Pb diffuse by a simple vacancy mechanism, is in agreement with Warburton on the basis of linear dehancement measurements of Hg in Pb,[22,23] with Miller on the basis of linear enhancement of Cd in Pb,[19] and with Miller and Edelstein's measurements of the isotope effect for Cd in Pb.[20] It is unfortunate that, as yet, no acceptable model exists for comparing the measured activation volume with multiple defect mechanisms, such as the interstitial-vacancy pair model.[21-23] It is obvious, however, that a mechanism more complex than simple vacancy diffusion is needed to explain the diffusion of Hg and Cd in Pb.

The activation volumes for Hg and Cd in Pb of 0.52 and 0.32 atomic volumes appear abnormally small for systems whose activation energies are so near to that for Pb self-diffusion. The measured value for the pressure correction due to heating of 1.6 kbar/100 °C tends to significantly decrease $\Delta V/V_0$ compared to what one would obtain for no pressure correction. A measurement was therefore made to determine if this pressure increase upon heating relaxed significantly during typical diffusion anneal times. The Sn I-II and the Sn II-L transitions were monitored over a period of 22 h while maintaining a pressure of about 47 kbar and 400 °C. The hydraulic load oil pressure relaxed as usual by about 3% during the first hour and then increased to its original value after about 6 h as the hydraulic oil warmed up due to the high cell temperature. The cell pressure however showed a maximum variation of less than 0.5 kbar which is within the experimental uncertainty. The small activation volumes for Hg and Cd in Pb appear to be real and not the result of our pressure calibration procedures.

The activation energies as reported here for the diffusion of Hg and Cd in Pb are larger than those reported by Warburton[23] and Miller[19] by 0.40 and

0.94 kcal/mole, respectively, with no overlap of the error flags of the corresponding measurements. Subsequent reanalysis of Miller's data for the pressure-independent diffusion parameters gave $D_0 = 1.1$ cm^2/sec, $\Delta H = 22.35$ kcal/mole, and $\Delta C_p/R = 5.2$ which are very close to, and within the quoted uncertainties of the values from Table I. The nonzero value of ΔC_p yields a temperature-dependent activation energy which produces a nonlinear Arrhenius curve. A plot of Eq. (2) with the above parameters was found to give a very excellent fit to Miller's zero-pressure data. This supports the Gilder and Lazarus proposal[27] that diffusion based on kinetic theory and equilibrium thermodynamics may yield nonlinear Arrhenius curves as a result of nonzero pressure and/or temperature coefficients of the activation volume.

ACKNOWLEDGMENTS

We would like to thank J. W. Miller and W. K. Warburton for the use of their atmospheric-pressure data for the diffusion of Cd in Pb and Hg in Pb, respectively.

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*Research supported in part by the NSF.

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