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Diffusion of Pd in Pb at high pressures*

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The diffusion of ^{109}Pd in Pb has been found to be very rapid with $D = (3.4 \pm 0.6) \times 10^{-3} \exp(-0.367 \pm 0.009\ \mathrm{eV}/kT)\ \mathrm{cm^2/sec}$. The activation volume for diffusion is only 0.04 ± 0.02 atomic volumes, indicating a very small effect of pressure on this diffusion. The pressure and temperature derivatives of the activation volume, $\Delta V/V_0$, are $(2.6 \pm 0.5) \times 10^{-3}\ \mathrm{kbar^{-1}}$ and $(0.9 \pm 0.4) \times 10^{-4}\ \mathrm{K^{-1}}$, respectively. These results, coupled with those from seven other tracers diffusing in Pb, have been analyzed in terms of an equilibrium model of interstitial, substitutional, and interstitial-vacancy pair defects. The analysis predicts the defects of Cu and Au in Pb to be primarily interstitial, Ni and Pd primarily interstitial-vacancy pairs, and Cd and Hg primarily substitutional.

I. INTRODUCTION

Rapidly diffusing impurities in high-Z polyvalent metals have been of interest since the early work of Roberts-Austen[1] and Seith and co-workers[2,3] who found the diffusivity of Au and Ag in Pb to be several orders of magnitude more rapid than Pb self-diffusion. It was subsequently concluded that these impurities must diffuse interstitially[4] in Pb. More recently, however, renewed interest in these rapidly diffusing impurities, along with more definitive experiments, such as linear enhancement,[4-7] isotope effects,[8,9] high-pressure measurements,[10-13] internal friction,[14,15] and effective-charge measurements[16,17] have indicated that the mechanism of diffusion is more complex than had originally been thought and may include contributions from two or more types of defects.

Miller[18] and Warburton,[19] in attempts to understand the relatively rapid diffusivity of Cd and Hg in Pb, have postulated a dissociative model involving substitutional, interstitial, and interstitial-vacancy pair defects. They concluded that the interstitial-vacancy pairs accounted primarily for the diffusivity[20,21] of Cd and Hg in Pb. Miller[5] concluded, on the basis of linear-enhancement measurements, that the diffusivity of Ag in Pb is controlled by interstitials with less than 20% contribution from an interstitial-vacancy pair mechanism.

Jeffery and Huntington,[16] looking at the electromigration of Au in Pb, find the measured effective charge does not clearly correspond to either pure vacancy or interstitial diffusion, thus suggesting a multiple mechanism of diffusion. Warburton[6] found a dehancement of Au diffusivity in Pb(Au) alloys, which he interpreted in terms of a defect consisting of pairs of Au atoms.

High-pressure measurements in this laboratory on the diffusivity of Ag,[10] Au,[11] Cu,[12] Ni,[13] Cd,[22] Zn,[23] and Hg,[24] in Pb suggest a multiple mechanism may be involved. Activation volumes for the diffusion of noble metals in Pb range from 0.16 to 0.35 atomic volumes. This suggests that the diffusivity of the noble metals in Pb cannot be explained by a single simple mechanism. The rapid diffusion of Ni in Pb, with its small activation energy and volume, precipitated the study of the diffusion of Pd in Pb which will be reported here.[25] The results of an analysis[26] will be presented, in which an attempt was made to correlate the measured diffusivities, activation energies, and volumes for eight different elements diffusing in Pb with a three-defect dissociative mechanism involving substitutional, interstitial, and interstitial-vacancy pair defects. The differences in diffusion are then interpreted in terms of the equilibrium fraction of each type of defect.

II. EXPERIMENTAL PROCEDURE

Following the experimental procedures described by Candland, Decker, and Vanfleet,[12] a total of 30 usable diffusion measurements were made for temperatures ranging from 200 to 590 °C at mean pressures of 1 bar and 20, 30, and 40 kbar. One end of each cylindrical Pb crystal was chemideposited with ^{109}Pd from an acidified radioactive-palladium-nitrate solution prior to the high-pressure anneal.

Samples were then suspended in petroleum ether within a pressure cell similar to that described by Curtin *et al.*[10] These samples were then annealed after being brought to the desired pressure in a tetrahedral anvil press. Liquid-scintillation-counting techniques made possible the efficient detection of the low-energy β particles emitted from the ^{109}Pd tracer. The procedure was the same as that described by Candland and Vanfleet.[13]

III. METHOD OF ANALYSIS

The analysis of diffusivity measurements as a function of temperature and pressure is generally reported in terms of a single effective mechanism of diffusion. This representation can be justified for a multiple diffusion mechanism if the contributing defect concentrations are in thermal equilibrium with each other at all penetrations. However, it must be realized that the measured or effective diffusivities, activation energies, and volumes must then be interpreted in terms of the diffusivities, energies, and volumes of the proposed model.

The measured or effective diffusion coefficient $D(P, T)$ for a single effective mechanism of diffusion based on kinetic theory and equilibrium thermodynamics leads to an expression of the form[11]

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

where f is the correlation factor and a is the lattice parameter (a constant for our experiment since all samples were sectioned at 1 bar and 23 °C).[27] 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 about $P=0$ and $T=T_0=600$ K and the coefficients in the expansions determined by a least-squares fit of Eq. (1) to all of the diffusion data simultaneously. In this way, one obtains the effective pre-exponential factor

$$D_0(0,T_0)=fa^2\,\nu(0,T_0)e^{\Delta S(0,T_0)/k}, \tag{2}$$

the activation energy or enthalpy $\Delta H(0, T_0)$, the activation volume $\Delta V(0, T_0)$, and the temperature and pressure derivatives of the activation volume. The pressure and temperature dependence of the correlation factor was not included in this analysis because it appeared that the resultant variation would fall well within the experimental uncertainty. This can be shown to be a reasonable assumption since this factor involves ratios of mode frequencies which will vary only slightly with pressure and temperature. As an example, an assumed 10% variation in f over 50 kbar would contribute only 0.1 cm^3/mole in ΔV. This is well within the uncertainties of any activation volume measured to date.

It is also possible to obtain ΔC_p, the specific heat of activation, if accurate measurements are made over a sufficiently large temperature range. It should be noted that a nonzero value of ΔC_p gives rise to a temperature-dependent activation energy and hence to nonlinear Arrhenius curves.

The calibration of the high-pressure hydrostatic cell, along with the pressure and temperature corrections and uncertainties, is described and discussed by Jorgensen.[24]

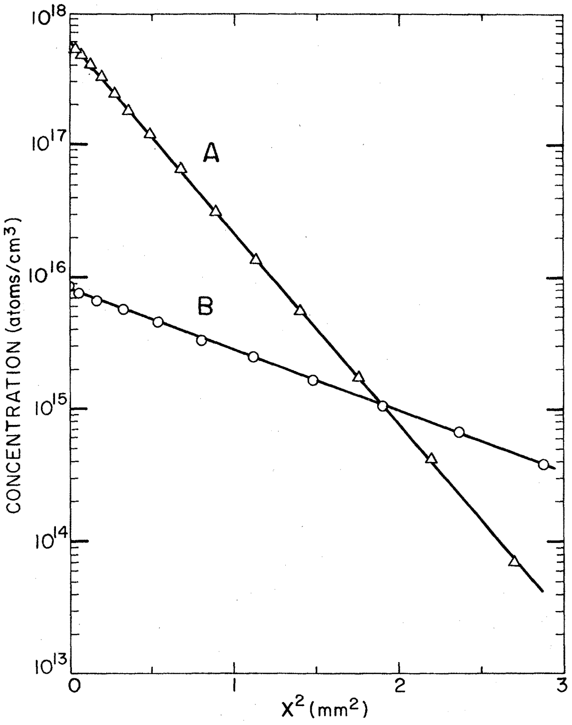

FIG. 1. Solute concentration profiles for the diffusion of Pd in Pb. Sample A was annealed at atmospheric pressure and 312 °C for 5.2 min, and sample B was annealed at 41.3 kbar and 528 °C for 8.0 min.

IV. RESULTS

Concentration profiles for two typical samples are shown in Fig. 1. Sample A was annealed at atmospheric pressure and 312 °C for 5.2 min, whereas B was annealed at 41.3 kbar and 528 °C for 8.0 min. The concentration profiles for the high-pressure anneals generally extended over one less order of magnitude than similar runs at atmospheric pressure. This difference in range was the result of having to use smaller samples for the high-pressure runs. It should be noted that all penetration profiles were Gaussian in shape, similar to that shown for samples A and B.

The diffusion coefficients for Pd in Pb as a function of reciprocal temperature are shown in Fig. 2 for pressures of 1 bar, 19.9, 29.7, and 39.9 kbar.

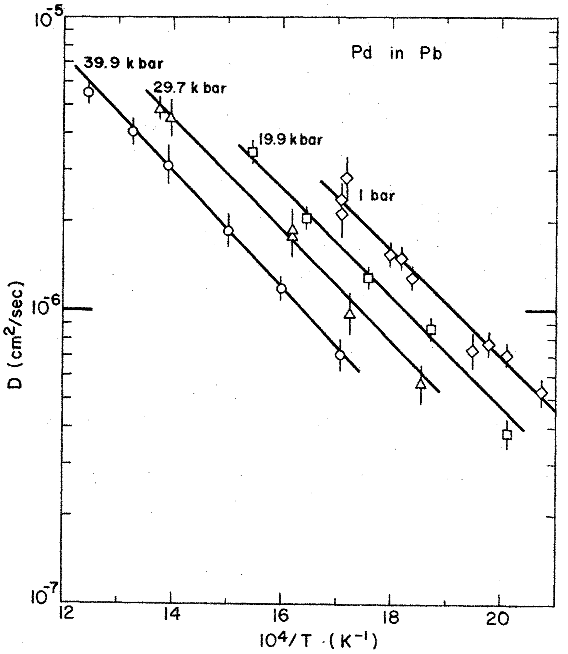

FIG. 2. Variation of diffusivity with inverse temperature for Pd in Pb along selected isobars.

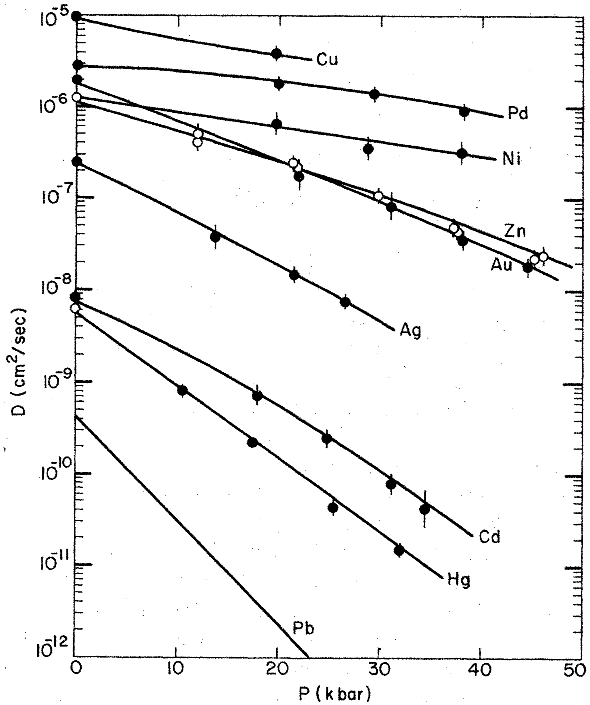

FIG. 3. Variation of diffusivity with pressure at 600 K for Cu, Pd, Au, Ni, Zn, Ag, Cd, Hg, and Pb in Pb.

Because of the temperature dependence of the pressure calibration no two high-pressure samples were annealed at exactly the same pressure. Hence the high-pressure data were corrected to isobars for displaying in the graph. This adjustment, which was in all cases less than 1.7 kbar, was accomplished using the best-fit parameters from all the data and the expansion of Eq. (1). The somewhat larger scatter in the atmospheric pressure data was the result of having to use a less sophisticated temperature control system as compared to that used for the high-pressure data.

The diffusion coefficients for Pd in Pb as a function of pressure are shown along the 600-K isotherm in Fig. 3. Corresponding diffusion data for Cu, Ni, Zn, Au, Ag, Cd, and Hg in Pb, along with the results for Pb self-diffusion,[20,21,28] are also shown. The solid lines represent this isotherm calculated from the best fit to all the data to Eq. (1).

Table I shows the experimental values for the pre-exponential factor D_0, the activation energy ΔH, and activation volume per atomic volume $\Delta V/V_0$, and the pressure and temperature derivatives of the activation volume for the diffusion of Pd in Pb. Note that D_0, ΔH, and ΔV are functions of temperature and/or pressure and have been tabulated for various temperatures and pressures. Recently, we have determined the pressure increase in our liquid cell as the temperature of the cell is increased to the diffusion-anneal temperature at constant press load.[24] This result differs from that estimated in our earlier work[10-13]; so

TABLE I. Measured parameters for the diffusion of palladium in lead.

(P,T) (kbar, K)	$D_0(P,T)$ (10^{-3}cm^2/sec)	$\Delta H(P,T)$ (eV)	$\Delta V/V_0$	$\frac{\partial(\Delta V/V_0)}{\partial P}$ (10^{-3}/kbar)	$\frac{\partial(\Delta V/V_0)}{\partial T}$ (10^{-4}/K)
(0 600)	3.4 ± 0.6	0.367 ± 0.009	0.038 ± 0.013	2.6 ± 0.5	0.9 ± 0.4
(25 600)	2.4	0.375	0.103		
(25 775)	2.4	0.375	0.117		
(50 600)	1.5	0.414	0.168		
(50 925)	1.5	0.414	0.197		

we have reanalyzed all our former measurements using a more accurate pressure calibration. A summary is given in Table II.

V. DISCUSSION

A comparison of the diffusion of Pd with the diffusion of Cu and Ni impurities in Pb show several similarities which suggest a pure interstitial mechanism primarily because of their small activation energy and volume. However, considering the accumulated results shown in Fig. 3, one is struck with the fact that the diffusivities of Cu, Pd, Ni, Zn, Au, Ag, Cd, Hg, and Pb in Pb are almost continuously distributed in regard to activation energy and volume between the extremes of Cu in Pb and Pb self-diffusion. It is difficult to imagine a single mechanism being responsible for this great variation in diffusivity, which ranges over more than four orders of magnitude. Even those impurities which have a relatively small activation volume and energy differ enough to question the concept of one responsible mechanism. Comparing Ni and Pd, which are in the same column of the Periodic Table, one finds a smaller activation energy for Pd and an activation volume about $\frac{1}{3}$ as large as for Ni. The pressure derivative of ΔV is also of opposite sign. This last fact is interesting in light of Weyland's[29] observation that, from Frank and Turnbull's[30] dissociative mechanism, the sign of the derivative of ΔV was dependent on the ratio of interstitial to substitutional impurities. Therefore, an attempt was made to correlate the high pressure data for the diffusivities of Ni and Pd, along with the noble metals in Pb, with the dissociative model by varying the equilibrium ratio of interstitial and substitutional impurities. No consistant result could be obtained for all of these impurities.

Miller,[18] in an attempt to understand the diffusion of Cd in Pb, extended Frank and Turnbull's dissociative model to include bound interstitial-vacancy pairs. He concluded that Cd in Pb diffused primarily by interstitial-vacancy pairs with little or no contribution from substitutional or interstitial defects. Miller's calculations were valid only for the case where the fraction of impurities as free interstitials q, and as pairs p, was much less than unity. Decker and Vanfleet[26] extended the calculations to include all values of p and q. The high-pressure diffusion data were fit to this later model. Following Miller one has

$$D=(1-q-p)D_s+qD_i+pD_p, \tag{3}$$

where q and p are the equilibrium fractions of impurities as free interstitials and pairs, respectively, and the subscripts s, i, and p refer to pure substitutional, interstitial and pair diffusion. In terms of energy states, the fractions p and q can be expressed by

$$\begin{aligned} p&=6e^{-Q/kT}/(1+e^{-I/kT}+6e^{-Q/kT}),\\ q&=e^{-I/kT}/(1+e^{-I/kT}+6e^{-Q/kT}), \end{aligned} \tag{4}$$

where I is the energy of a free interstitial and Q is the energy of an interstitial-vacancy pair relative to a substitutional impurity. Note that $Q=I+g_v+B$ in Miller's notation, where g_v is the energy to form a vacancy, and B is the binding energy between the interstitial and vacancy.

The effective activation energy and volume are found by taking logarithmic derivatives of the effective diffusion coefficient with respect to temperature and pressure and are given by

$$\begin{aligned} \Delta H=&(1-p-q)(\Delta H_s-qI-pQ)D_s/D\\ &+p[\Delta H_p-qI+(1-p)Q]D_p/D\\ &+q[\Delta H_i+(1-q)I-pQ]D_i/D, \end{aligned} \tag{5}$$

$$\begin{aligned} \Delta V=&(1-p-q)(\Delta V_s-q\Delta V_{is}-p\Delta V_{ps})D_s/D\\ &+p[\Delta V_p-q\Delta V_{is}+(1-p)\Delta V_{ps}]D_p/D\\ &+q[\Delta V_i+(1-q)\Delta V_{is}-p\Delta V_{ps}]D_i/D, \end{aligned} \tag{6}$$

TABLE II. Summary of high-pressure measurements of diffusion in lead evaluated at zero pressure and 600 K.

Isotope	D (10^{-8}cm^2/sec)	D_0 (10^{-2}cm^2/sec)	ΔH (eV)	$\Delta V/V_0$	$\frac{\partial(\Delta V/V_0)}{\partial P}$ (10^{-3}/kbar)	$\frac{\partial(\Delta V/V_0)}{\partial T}$ (10^{-4}/K)
^{64}Cu	912	0.86 ± 0.09	0.354 ± 0.007	0.16 ± 0.02	−2.9 ± 1.7	0.8 ± 0.8
^{109}Pd	280	0.34 ± 0.06	0.367 ± 0.009	0.04 ± 0.02	2.5 ± 0.9	0.9 ± 0.7
^{197}Au	182	0.58 ± 0.07	0.417 ± 0.006	0.27 ± 0.02	0.7 ± 1.6	−1.8 ± 0.7
^{63}Ni	133	1.9 ± 0.8	0.495 ± 0.029	0.13 ± 0.02	−1.0 ± 1.3	1.4 ± 1.3
^{65}Zn	112	1.65 ± 0.2	0.496 ± 0.007	0.21 ± 0.01	1.2 ± 0.6	−0.7 ± 0.4
^{110}Ag	24.8	4.8 ± 0.5	0.630 ± 0.006	0.35 ± 0.02	1.9 ± 1.7	−2.7 ± 0.8
^{109}Cd	0.75	42 ± 9	0.924 ± 0.010	0.32 ± 0.02	4.9 ± 1.5	2.2 ± 1.2
^{203}Hg	0.57	143 ± 17	1.000 ± 0.005	0.51 ± 0.03	−0.3 ± 0.6	0.2 ± 0.3

where ΔV_{is} and ΔV_{ps} are the derivatives of I and Q with respect to pressure, and the other energies and volumes correspond to pure substitutional, interstitial, and pair diffusion according to the subscripts.

Assuming that the diffusion of these tracers in lead is characterized primarily by the equilibrium fractions p and q, one can from the present data, estimate the p's and q's for each as well as the parameters D_i, ΔH_i, ΔV_i, ΔV_{is}, D_p, ΔH_p, ΔV_p, and ΔV_{ps}. The remaining parameters D_s, ΔH_s, and ΔV_s were chosen to correspond to the respective values measured for self-diffusion. The assignment is justified by the fact that the charge of those atoms is likely completely screened in polyvalent lead at the nearest neighbor distance.[31] The measured values of D, ΔH, and ΔV, for the eight tracer experiments, all evaluated at atmospheric pressure and 600 K, coupled with Eqs. (3), (5), and (6), gave 24 nonlinear equations in 24 unknowns. These were algebraically reduced to eight equations with eight unknowns and then solved by computer using a nonlinear least-squares-fitting technique[32] to yield the results in Table III. Although the assumption that the diffusion parameters are independent of the diffusing impurity may be questioned, the p's and q's, along with the corresponding energies I and Q, seem very reasonable and are close to what one might have expected. The results indicate that Cu dissolves almost entirely as an interstitial impurity, whereas Au and Ag have a decreasing interstitial fraction. Palladium and Ni have larger pair fractions than interstitial, whereas Cd and Hg form primarily substitutional alloys with less than 1% contribution from pairs or interstitials.

In calculating the isotope effect for this model, we realized that there must be a mass dependence for the D_s, D_i, and D_p in Eq. (3), so we included such an effect and repeated the least-squares fitting. The results were not substantially different from those given in Table III, except for the case of Cu, where q dropped from 0.98 to 0.7 and p increased to 0.3. The isotope calculations yielded values that were much too large,[8,9,33] unless we assumed the isotope effect for the interstitial motion to be ≃0.25. This would indicate a correlated motion of several atoms in the interstitial jump.

TABLE III. Parameters for the substitutional, interstitial, and interstitial-vacancy-pair dissociative mechanism determined from diffusion measurements of eight impurities in lead and the equilibrium fractions of interstitial, q, and pair type p defects for these impurities. The energies Q and I are calculated from Eqs. (4).

Impurity	p	q	Q (eV)	I (eV)
Cu	0.01	0.98	0.08	−0.22
Pd	0.54	0.28	0.04	−0.02
Au	0.05	0.18	0.21	0.07
Ni	0.65	0.11	0.04	0.04
Zn	0.45	0.10	0.09	0.08
Ag	0.06	0.024	0.23	0.19
Cd	0.0003	0.0008	0.52	0.37
Hg	0.002	0.0004	0.40	0.40

$D_i/D_s = 20\,660 \pm 40$ $D_p/D_s = 1300 \pm 100$

$\Delta H_i = 0.354 \pm 0.001$ eV $\Delta H_p = 0.90 \pm 0.06$ eV

$\Delta V_i/V_0 = 0.165 \pm 0.005$ $\Delta V_p/V_0 = 0.65 \pm 0.10$

$\Delta V_{is}/V_0 = 0.110 \pm 0.005$ $\Delta V_{ps}/V_0 = 0.57 \pm 0.03$

The parameters in Table III, when used with Eqs. (3), (5), and (6), yield $D(0, 600\,°\mathrm{K})$ to within ±3%, $\Delta V/V_0$ to within ±0.02, and gave values of ΔH to within ±8% of the measured values. It is also interesting to note that in spite of the fact that Eq. (3) involves the sum of three different exponential factors (D_s, D_i, and D_p), a plot of the theoretical values of $\ln D$ versus $1/T$ is linear to within a few percent for all the materials reported in this work over the temperature range of the measurements. Part of the reason for this might be due to the temperature dependence of the p's and q's, which is shown explicitly in Eq. (4), or to the dominance of the interstitial term in the diffusion rate of these materials.

Although the analysis has been done for substitutional, interstitial, and pair-type defects, the theory, with very little change, would accommodate other types of defects. For example, the impurity-impurity and impurity-host diplons as proposed by Warburton[34] could be used equally well with only minor changes. These changes would involve merely a redefinition of Q and I and would replace the 6 in Eq. (3) with a different number because of different probabilities in the distributions.

We conclude that the diffusion of Pd in Pb is very rapid and is nearly independent of pressure, but that it takes place by a mechanism which is quite different than that of copper, which appears to be essentially by free interstitials. This diffusion of Pd in Pb can be explained in terms of a large contribution from interstitial-vacancy pairs with some free interstitials. In this feature, it is quite similar to the diffusion of Ni in Pb. It would help to have enhancement experiments on the diffusion of Pb in a Pb(Pd) alloy, for we would expect a very different result for pair diffusion, which is enhanced similar to a direct interchange mechanism, and interstitial diffusion, which should show little if any enhancement. The most puzzling thing is the small activation volume which is considerably smaller than that for free interstitial or pair diffusion alone. Apparently, some of the major terms in Eq. (6) must be of opposite sign, and cancel to give this result. Under these circumstances, it surely could not be interpreted in the usual way as an activation volume of some particular mechanism. This analysis may be too naive in letting D_i, D_s, and D_p be independent of the impurity. This is justified only for D_s.

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