

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 $D = (3.4 \pm 0.6) \times 10^{-3} \exp(-0.367 \pm 0.009 \text{ eV/kT}) \text{ cm}^2/\text{sec}$. 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 $(2.6 \pm 0.5) \times 10^{-3} \text{ kbar}^{-1}$ and $(0.9 \pm 0.4) \times 10^{-4} \text{ K}^{-1}$, 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-Austen¹ 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 interstitially⁴ 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.

Miller¹⁸ 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. Miller⁵ 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. Warburton⁶ found a deenhancement 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 analysis²⁶ 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 form¹¹

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

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

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

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 cm³/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

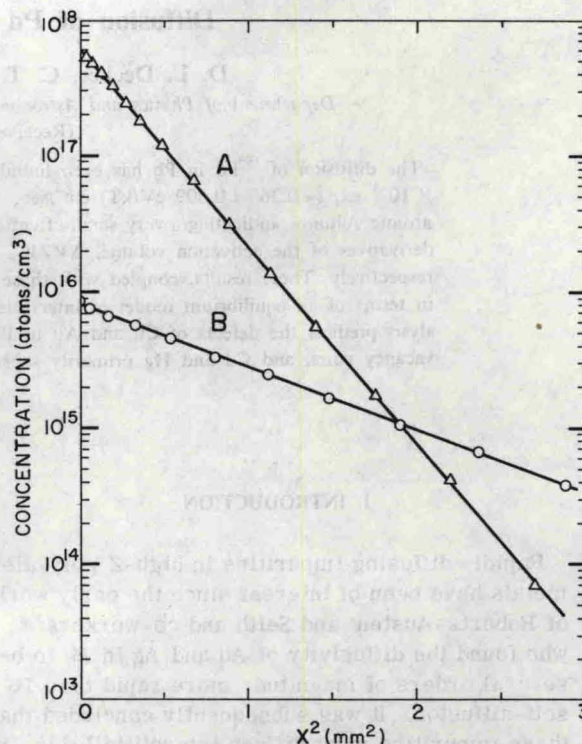


FIG. 1. Solute concentration profiles for the diffusion of Pd in Pb. Sample A was annealed at atmospheric pressure and 312 °C for 5.2 min, and sample B was annealed at 41.3 kbar and 528 °C for 8.0 min.

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

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.