

FIG. 5. Penetration profiles of Au diffusion in lead at 132.2 °C for 4 h 36 min and at 60.4 °C for 47 h 46 min.

gold concentration everywhere very low to prevent tracer de-enhancement. Two of these diffusion profiles are shown in Fig. 5 and a summary of all diffusion measurements of the diffusion of Au in Pb are displayed in Fig. 6.^{3,6,23,24} An analysis of our diffusion measurements of Au in pure lead over the range 60 to 300 °C yielded the results: the pre-exponential factor $D_0 = (5.2 \pm 0.3) \times 10^{-3}$ cm²/sec, the activation energy $Q = 9230 \pm 70$ cal/mole, and the diffusion constant at the melting temperature of lead $D_{\text{melt}} = (2.265 \pm 0.029) \times 10^{-6}$ cm²/sec.

DISCUSSION AND CONCLUSIONS

It has been assumed that the diffusion of gold in lead is dominated by interstitial diffusion $D = qD_i$, where q is the equilibrium fraction of interstitial gold and D_i is the rate of interstitial diffusion. This expression follows because we expect interstitial defects to diffuse much faster than substitutional defects. If one assumes the substitutional and interstitial-jump probabilities to be of about equal magnitude, then substitutional diffusion will be slower than interstitial diffusion by the vacancy concentration, about 1 part in 10^4 , at the melting point which corresponds to the probability of find-

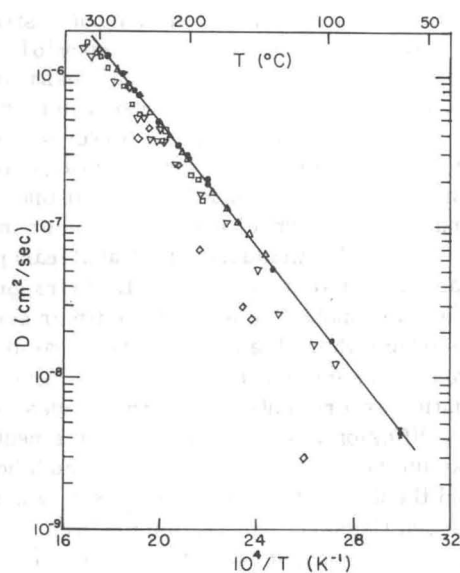


FIG. 6. Diffusivity of gold in lead (●) this work, (◇) Ref. 23, (▽) Ref. 24, (□) Ref. 3, (△) Ref. 6. Solid line is least-squares fit to present data.

ing a place available for a diffusion jump from one substitutional site to a neighboring site. The analysis by Decker *et al.*¹¹ (hereafter referred to as DCV) of eight separate solutes in lead determined a ratio of 4.8×10^{-5} for D_s/D_i at 600 K which is in good agreement with the above argument. From the temperature dependence of q one would expect qD_i to be nearly Arrhenius over the temperature range 60 to 300 °C with a small deviation from Arrhenius behavior appearing near the melting point. At lower temperatures, however, the fraction of interstitials q will become so small that qD_i is no longer the dominant mechanism for diffusion, and substitutional diffusion will be important. This will cause a change in slope in the $\ln D$ -vs- $1/T$ curve because of the different activation energy for substitutional diffusion. From the temperature dependence of the q and the D_i and D_s in DCV we predict that the substitutional diffusion will only dominate below 50 K, so we expect essentially Arrhenius behavior as is verified by the present data in Fig. 6. We conclude that interstitial diffusion dominates the diffusion of Au in Pb from the melting temperature to at least 60 °C and that previously measured values of gold diffusivity in lead, which fall well below the present values as shown in Fig. 6, are due to de-enhancement effects involving impurities in the lead or tracer de-enhancement due to the concentration of the diffusing gold.

At 60 °C the diffusion penetration profile was not Gaussian but had a shape approaching an error function. The measurement at 132 °C however was accurately Gaussian. At 96 °C the profile showed de-

viation from Gaussian behavior but not as strongly as at the lower temperature. The tendency to be non-Gaussian at lower temperatures has been noted many times previously and was assumed to stem from surface or saturation problems.^{3,25} However, we successfully went to a much lower temperature before losing a Gaussian response by the use of only minute amounts of a high-specific-activity tracer and a high-purity host. This would indicate that at least part of the profile problem might be related to trapping of the tracer in immobile substitutional dimer states near the surface where the concentration may be large. Barbu,²⁵ in some interesting thermal neutron-irradiation experiments, restored a Gaussian profile to Au diffusion in lead. Apparently the neutrons broke up the substitutional dimers which both reduced the de-enhancement coefficient to zero and produced Gaussian penetration profiles. Using thermal neutrons, defects in the lead such as Pb interstitials were probably not produced.

It has been reported that Au impurities⁶ in Pb strongly de-enhance the diffusivity of Au in Pb but that Ag impurities¹⁵ do not significantly affect Ag diffusion in Pb. We observe that the diffusion of Au in lead is also strongly retarded by small amounts of Pd in the lead host and, to a smaller extent, by Ag impurities. The results, especially for the Ag alloys for which the effect is smaller, show more scatter than one would expect from the estimated uncertainties in the measurement of $D(x)$. We traced this problem to the different times spent by the samples at room temperature while awaiting their turn for sectioning. An attempt was made to correct for this but could not be accurately accomplished. We did note that $D(0)$ for three pure samples all with identical anneal histories was slightly smaller as the time at room temperature, following the anneal, increased as if some back diffusion had taken place. This effect was much smaller for the alloy samples. The effect is very small but none the less large enough to cause the observed scatter in the data.

We agree with Warburton⁶ that the existence of de-enhancement indicates that a bound state or polyatomic defect state of the impurities in lead must exist. Warburton argues for the necessity of substitutionally situated defects consisting of more than two impurity atoms at the same site. His original reasoning stemmed from a seeming incompatibility between the substitutional dimer model and his experimental results. He felt that his measured de-enhancement exceeded the predictions of the substitutional dimer model. We note that if one graphs $D(x)/D(0)$ as a function of $-2b_{21}x$ for each sample a universal curve for all measurements independent of temperature appears, as seen in Eq. (11). Warburton analyzed his data

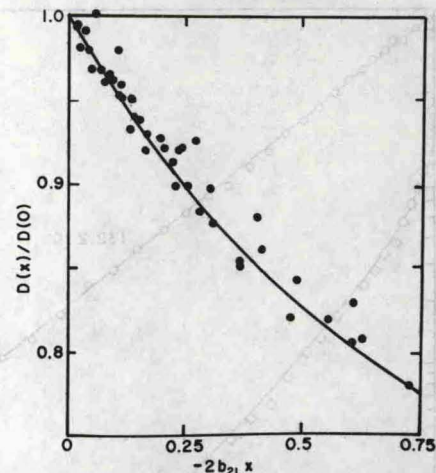


FIG. 7. Ratio of diffusivity of Au in Pb(Au) of concentration x to that in pure lead versus $-2b_{21}x$. The reanalyzed data of Ref. 6. (See text). The solid line is the theoretically expected curve of Eq. (11) with $a=2$.

assuming $D(x)/D(0) = 1 + b_{21}x$, rather than the complete expression as given in Eq. (11), to get values of b_{21} and found a deviation from the predicted universal curve. Our reanalysis of his data using the correct expression does not show any such deviation (see Fig. 7). In Fig. 8 we make the same type of plot for our data of Au diffusion into Pb alloyed with Ag or with Pd. We conclude that a simple model involving only single defects and substitutional dimers describes the observed de-enhancement data to within the accuracy of the data and there is no need to consider higher-order defect clusters. We also conclude that not only are Au-Au substitutional dimers found in lead but also Au-Pd and Au-Ag substitutional dimers.

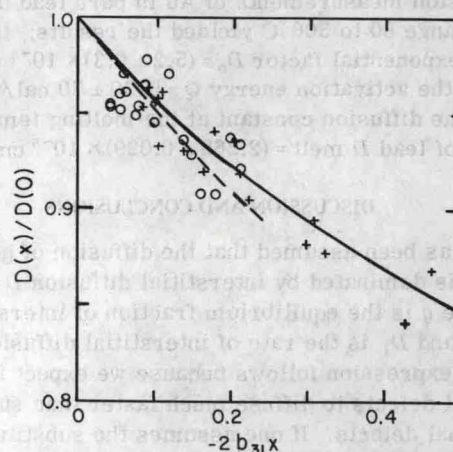


FIG. 8. Ratio of diffusivity of Au into Pb alloys to that of pure Pb (where x is the alloy concentration) as a function of $-2b_{31}x$. The solid line is the theoretical expression for Pb(Pd) alloys and the dashed line for Pb(Ag) alloys. (+) Pb(Pd) data, (O) Pb(Ag) data.