De-enhancement of gold diffusion in lead by impurities in the lead

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Measurements of the effects of alloying lead with silver and palladium on the diffusivity of gold in lead are reported. It is observed that both Pd and Ag strongly de-enhance Au diffusion in lead; in fact, the Pd de-enhances Au diffusivity in Pb more pronouncedly than alloying lead with gold. It was found that the binding energy between a Au tracer in an interstitial site and Pd, Au, or Ag atoms in substitutional sites to form substitutional dimers was the same in all three cases.

INTRODUCTION

Measurement of the diffusion of gold into lead has led to many surprises since the first measurements by Roberts-Austen.[1] The diffusion rate was found to be some five orders of magnitude faster than that of self-diffusion in lead[2] and was shown not to be a result of grain boundary or dislocation diffusion.[3] The activation volume for diffusion was observed to be intermediate to those expected for interstitial or substitutional diffusion.[4] Miller[5] observed the enhancement of Pb self-diffusion by gold to be too small for substitutional diffusion but too large for interstitial diffusion, and most recently Warburton[6] has observed a strong de-enhancement of gold diffusion in lead by gold impurities in the lead. A linear de-enhancement coefficient is defined by expanding the diffusivity as a power series in the concentration x of the impurity

$$D(x) = D(0)(1 + b_{21}x + b_{22}x^2 + \cdots) . \tag{1}$$

The experimental value of b_{21} for Warburton's measurements was as large as -3000 at $140\,^\circ$C. This means that as little as a 30-ppm gold concentration would reduce the diffusion rate of gold in lead by nearly 10%. To explain this result Warburton proposed that gold forms substitutional dimers or higher-order clusters in lead that are stable at lower temperatures. A substitutional dimer, as we define it here, is a defect in which two gold atoms exist together at a single substitutional site in the lead. One might extend this definition to include the possibility of two bound gold atoms that move together but do not need to occupy a given atomic site. This extension is not appealing because the screening in lead is so effective that electrostatic forces are basically screened even at nearest-neighbor separation.[7] We note that the gold ion is sufficiently small[8] to allow two of them to fit confortably in a single atomic volume in lead. Warburton felt that his de-enhancement measurements were not adequately represented by a simple substitutional dimer mod-

el so he suggested the existence of higher-order clusters also.

Many other impurities, such as Cu, Ag, Zn, Pd, Ni, and Pt, have been observed to diffuse very rapidly in lead.[9-14] The obvious next step was to look for the possible formation of substitutional dimers by these other defects in lead. Cohen and Warburton[15] did this for Ag in Pb and found very little to zero de-enhancement indicating little probability of Ag-Ag substitutional dimers forming in lead even though the Ag ions are about the same size as the Au ions. One might look for de-enhancement in others of these impurity-lead diffusion couples,[16] but because of the ease of measuring gold diffusion in Pb with the availability of extremely high specific-activity Au isotopes we decided first to look for de-enhancement of gold diffusivity in lead by the presence of others of these impurity atoms which diffuse rapidly in lead.

THEORETICAL ANALYSIS

In this section we will derive an expression for the de-enhancement of tracer diffusion by another impurity atom in the host. Let x be the concentration of the impurity and x^* that of the tracer. Let c_i, c_s, and c_d stand for the concentrations of impurity atoms in interstitial, substitutional, and substitutional dimer states, respectively, and let c_i^*, c_s^*, and c_d^* represent the same for the tracer. The concentration of vacancies is given by c_v and the concentration of tracer-impurity substitutional dimer is c_d^*. The following reactions may then take place:

$$
\begin{array}{cccc}
 & k_5 & & \\
d & d^* \rightleftarrows & s^* + i & d^{**} \\
k_4\,\updownarrow & k_3\,\updownarrow & \updownarrow k_2 & k_6\,\updownarrow \\
s \rightleftarrows i + v & s & i^* & s^* \\
k_1\,\big\downarrow & & & \\
+ & + & + & + \\
i & i^* & v & i^* .
\end{array}
$$
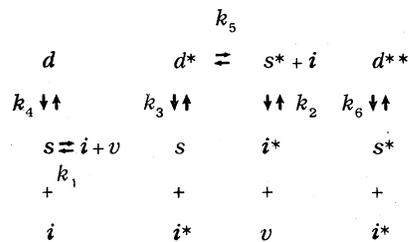
The k's in these reactions represent equilibrium constants. These reactions lead to the following

equations:

$$\frac{c_s c_i}{c_d} = k_4, \quad \frac{c_s c_i^*}{c_d^*} = k_3, \quad \frac{c_s^* c_i}{c_d^*} = k_5 ,$$

$$\frac{c_i c_v}{c_s'} = k_1, \quad \frac{c_i^* c_v}{c_s^*} = k_2, \quad \frac{c_s^* c_i^*}{c_d^{**}} = k_6 . \qquad (2)$$

In addition we must consider the two equations which describe the conservation of particles:

$$c_s^* + c_i^* + 2c_d^{**} + c_d^* = x^*$$

and   (3)

$$c_s + c_i + 2c_d + c_d^* = x.$$

It is readily recognized from Eq. (2) that the k's are not all independent, in fact, $k_5 = k_3 k_1/k_2$.

We now substitute Eq. (2) into Eq. (3) and introduce $q^* = c_i^*/x^*$ and $q = c_i/x$ to arrive at

$$1 + \frac{c_v}{k_2} + \frac{2q^* x^* c_v}{k_2 k_6} + \frac{q x c_v}{k_1 k_3} = \frac{1}{q^*} ,$$

$$\qquad \qquad \qquad \qquad \qquad \qquad \qquad (4)$$

$$1 + \frac{c_v}{k_1} + 2\frac{q x c_v}{k_1 k_4} + \frac{q^* x^* c_v}{k_1 k_3} = \frac{1}{q} .$$

The q and q^* represent the fraction of impurities and tracers that are in interstitial sites at equilibrium.

One could also include interstitial-vacancy pairs[17] in the theory. However, since these pairs are merely a step in the breakup of a substitutional state to an interstitial state and a vacancy, one arrives at the same expressions, Eq. (4), with slightly different definitions for k_1 and k_2.

In our case, because of the high specific activity of the tracer, x^* is very small everywhere and will not affect the diffusion so we assume $x^* = 0$ in Eq. (4). This assumption is justified *a posteriori* by the Gaussian diffusion profiles.[18] We now solve Eq. (4) to get

$$q^*(x) = q_0^* a/[a - 1 + (1 - 2ab_{31}x)^{1/2}] , \qquad (5)$$

with the following definitions:

$$q(0) = q_0 = (1 + c_v/k_1)^{-1}, \quad q^*(0) = q_0^* = (1 + c_v/k_2)^{-1}, \quad (6)$$

$$a = 4 k_3 q_0/k_4 q_0^* , \quad b_{31} = -c_v q_0 q_0^*/k_1 k_3 . \qquad (7)$$

If we assume that the diffusion rates of substitutional and substitutional dimer states are very slow compared to that of interstitial states, then[19]

$$D(x) = q^*(x) D_i , \qquad (8)$$

where D_i is the pure interstitial diffusion constant for the tracer. This expression is valid under the assumption that x^* is everywhere negligible.[18] Substituting Eq. (5) into Eq. (8) and expanding in a power series in x we get

$$D(x) = D_i q_0^* (1 + b_{31}x + \cdots) . \qquad (9)$$

Thus b_{31} is the linear solute de-enhancement coefficient which we label b_{31} to distinguish it from the linear self-solute de-enhancement coefficient which is called b_{21}. In other words, b_{21} is used when the tracer diffusion is de-enhanced by the same kind of atoms that constitute the tracer and b_{31} when the de-enhancement is caused by a third party of solute atoms. In the limit as the solute approaches the tracer, $k_2 \to k_1, k_6 \to k_4 \to 2k_3,$ and $q_0 \to q_0^*$ and we find

$$b_{21} = -2c_v q_0^{*2}/k_2 k_6 \quad \text{and} \quad a = 2 . \qquad (10)$$

In order to compare the experiments with the theory we note that with the substitution of Eq. (5) into Eq. (8) it becomes

$$D(x) = D(0) a/[a - 1 + (1 - 2abx)^{1/2}] . \qquad (11)$$

One then does a least-squares fit of the experimental data $D(x)$ at a constant temperature to this expression with the three parameters a, b, and $D(0)$. $D(0)$ is the diffusion rate of the tracer into a pure host, and b is the linear de-enhancement coefficient. We fit Warburton's de-enhancement of Au diffusing into Pb(Au) alloys to Eq. (11) with $a = 2$. This is equivalent to the expression derived by Warburton but not used by him to analyze his data.

EXPERIMENTAL PROCEDURES

Details of this procedure are given in Melville's dissertation.[20]

Diffusion measurements: Weighed amounts of 99.9999% pure lead were mixed with 99.999 % pure Ag or Pd, sealed under vacuum in a Pyrex tube, and then melted. This melt was stirred by agitation and then air cooled. The resulting ingots were remelted in a graphite mold under vacuum in a uniform-temperature furnace and then cooled to ambient temperature in about three hours. This procedure was developed to homogenize the Ag or Pd impurities in the Pb. Attempts to grow single crystals always resulted in concentration gradients along the rods. The samples were 4.8 mm in diameter and sliced into diffusion sections about 5 mm long after discarding the ends of the rod. Each diffusion measurement consisted of four samples, three of which were alloys, the fourth being a pure lead sample for reference. They were all plated from a ^{195}Au solution in HCl by dropping 25μl of solution on a freshly microtomed surface using a Hamilton gas-tight syringe with a plastic needle. After two minutes of plating, the remaining solution was removed with a Kimwipe dampened with NH_4OH and the surface was rubbed on paper saturated with methanol. The samples were then air dried and placed in the diffusion furnace

which was a tube of silicone oil in a liquid-metal bath whose temperature was held constant by a Tronac PTC 30 precision temperature controller. The four samples were clamped together with the plated faces in contact and a Chromel-Alumel thermocouple junction between the center two. They were moved up and down in the silicone fluid during the anneal to help maintain a uniform temperature over the four samples to within ±0.01 °C. Another advantage of this type of stirring was that it provided an 8 sec warm-up from ambient to the anneal temperature. At the close of the anneal the samples were quenched in water, one or two diffusion lengths were machined off the cylindrical surfaces with a lathe, and then they were sectioned in 20-μm sections beginning at the plated surface. The activity in each section was counted using a Tracerlab scintillation NaI well counter. About 2 mm were removed from each sample before the counting rate was reduced to background, then another 20-μm slice was removed from each sample and analyzed for Ag or Pd content using a differential scanning calorimeter.[21] The concentrations thus determined were always very near those expected from the weighed amount of starting materials.

A few low-temperature diffusion anneals were made of [195]Au diffusing into pure lead in the same manner as described above. The specific activity (carrier free) of the [195]Au was so high that an extremely small amount of gold was sufficient to trace the diffusion. This coupled with the purity of the lead should minimize tracer de-enhancement effects.

Solubility of Pd in Pb: It is important in the de-enhancement experiments to keep the impurity concentration below the solubility limit at the temperature of the anneal. For the Pb(Ag) alloys we have the work of Cohen and Warburton to guide us but the saturation solubility of Pd in Pb has never been measured. We measured this solubility using the resistivity technique described by Rossolimo and Turnbull.[22]

Pb (Pd) alloys prepared as above were extruded as 0.5-mm diameter wires of 60-cm length. An identical pure lead wire was also formed. The pure wire, along with each respective alloy wire, was wound in parallel on a double-threaded lava cylinder and placed in a uniform-temperature furnace. Current and potential leads of lead were attached to one end of each wire. Outside the furnace these leads were attached to copper wires. The other end of the samples were joined and a third potential lead of Pb attached at this point. A constant current was run in series through the samples and the ratio of the voltage across the impure sample to the total voltage across the two

was measured with a Hewlett-Packard 3420B differential voltmeter-ratiometer. The samples were slowly heated from room temperature to 300 °C in a nitrogen atmosphere and the output of the ratiometer recorded against the temperature read from a Chromel-Alumel thermocouple. For $\Delta R \ll R$ this output is proportional to $\Delta R/R$.

RESULTS

To determine the solubility of Pd in Pb we measured the ratio of the resistance of a Pb(Pd)-alloy wire to the sum of the resistances of this wire and a pure lead wire of the same dimension as a function of temperature. The results for a Pb(Pd) alloy with 289 ppm Pd are shown from an XY recorder in Fig. 1. The temperature T_s above which the Pd is dissolved in the Pb is shown in the figure. In this manner four Pb(Pd) alloys were measured and the temperature dependence of the solubility is shown in Fig. 2 in conjunction with former measurements on Pb(Ag) and Pb(Au) alloys.

The de-enhancement measurements were analyzed as standard tracer-diffusion profiles with the gold diffusing from the plated surface into the lead alloys of various alloy concentrations. A group of samples all passing through the same thermal history were plated, diffused, sectioned, and counted. In Fig. 3 we show a typical set of penetration profiles for Pb(Pd) alloys all diffusing at 256 °C. From the slopes of these curves one obtains the diffusion constants $D(x)$ and dividing this into $D(0)$, taken from the pure sample diffusion slope in each set, we get a ratio $D(0)/D(x)$ for each alloy concentration. In this manner 19
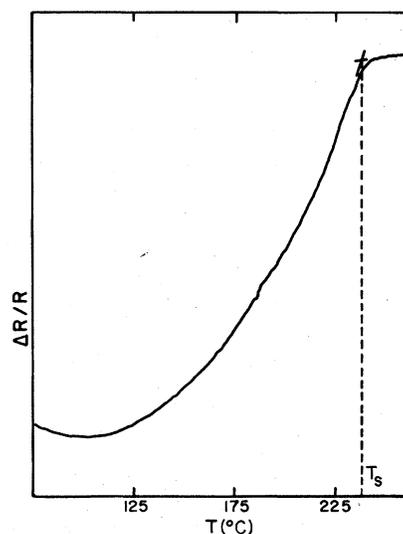
FIG. 1. Impurity resistance of 289-ppm Pd in Pb as a function of temperature. T_s is the temperature at which Pb is saturated with 289 ppm Pd.
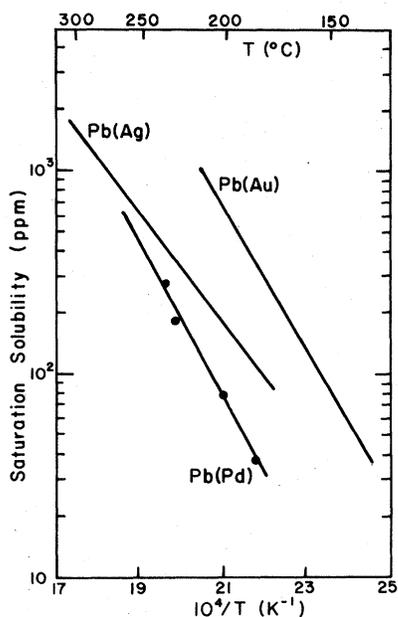
FIG. 2. Saturation solubility in atomic parts per million (ppm) of Pd, Ag, and Au in Pb as a function of temperature.
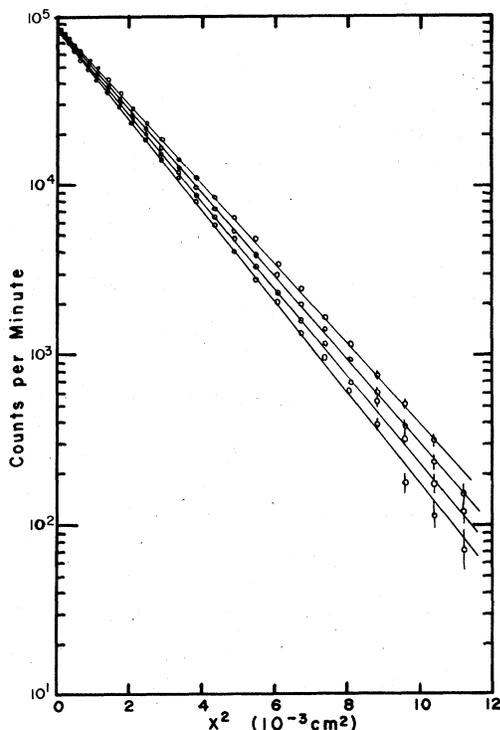
FIG. 3. Penetration profiles for Pb(Pd) alloys annealed at 256 °C for 590 sec. The curves starting from the top correspond to alloys containing 0, 87, 187, and 269 ppm Pd.
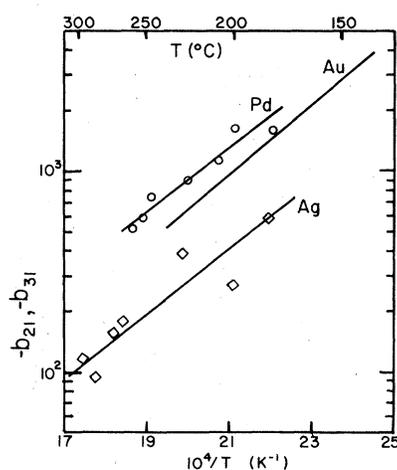
FIG. 4. Linear de-enhancement coefficient for the de-enhancement of Au diffusing in Pb alloyed with Pd, Au, and Ag. The measurements with Pd ($\bigcirc$) and Ag ($\square$) are reported herein and the Au results are taken from our analysis of data in Ref. 6.

ratios for Au diffusing in Pb(Pd) alloys at temperatures between 181° and 263 °C and 19 ratios for Au diffusing in Pb(Ag) alloys at temperatures between 182 ° and 300°C were measured. The data for the Pd alloys was then fit by least-squares analysis to Eq. (11) assuming a to be independent of temperature and letting b_{31} be of the form $b_{31}(T) = -C_1 \exp(C_2/T)$. The Arrhenius form for b_{31} follows from Eqs. (6) and (7) whenever $k_1/c_v = c_i/c_s \ll 1$ and $k_2/c_v = c_i^*/c_s^* \ll 1$, which in turn seems to be justified by Decker et al.[11] This analysis yielded $a = 3.6 \pm 1.5$ and $b_{31} = (-0.54 \pm 0.33)$ $\exp[(3710 \pm 310)/T]$. The data for the Ag alloys had too much scatter to give a meaningful determination of a so we assumed $a = 0.19$ as explained in the discussion section and then C_1 and C_2 were determined by the least-squares analysis. In this manner we found $b_{31} = (-0.17 \pm 0.14) \exp[(3730 \pm 650)/T]$. In Fig. 4 we have plotted b_{31} as a function of temperature for the de-enhancement of Au diffusion in Pb(Ag) and Pb(Pd) alloys from the C_1 and C_2 obtained above.

We also reanalyzed the 56 data points of Warburton for Au diffusing in Pb(Au) alloys using a least-squares fit to Eq. (11) with $a = 2$ and assuming the above temperature dependence of b_{21} yielding

$$b_{21} = (-0.32 \pm 0.10) \exp[(3810 \pm 180)/T].$$

These results are also shown in Fig. 4.

Finally, because of the suggestion that low-temperature diffusion of gold in lead was not just an extension of the high-temperature data, we made three low-temperature diffusion measurements at 132, 96, and 60°C, respectively, using a high-specific-activity gold tracer to keep the
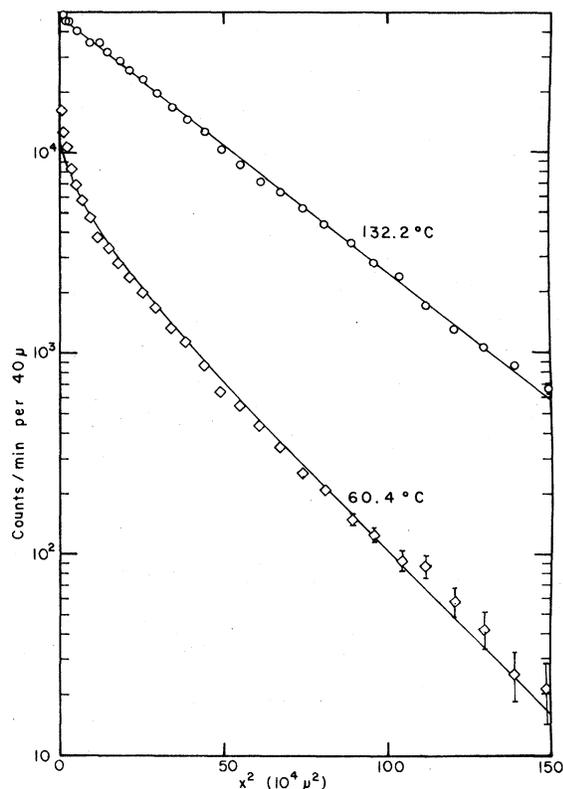
FIG. 5. Penetration profiles of Au diffusion in lead at 132.2 °C for 4 h 36 min and at 60.4 °C for 47 h 46 min.

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.

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 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-

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 impurities[6] in Pb strongly de-enhance the diffusivity of Au in Pb but that Ag impurities[15] 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 Warburton[6] 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
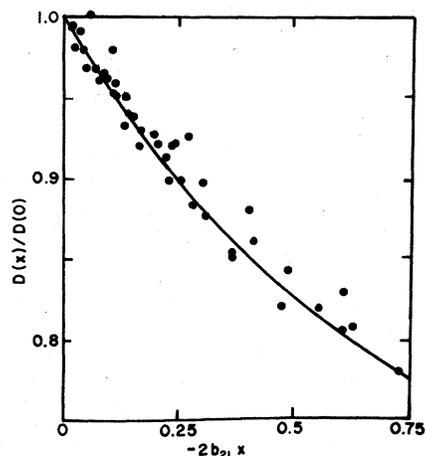
FIG. 7. Ratio of diffusivity of Au in Pb(Au) of concentration x to that in pure lead versus $-2b_{21}x$. The reanalyzed data of Ref. 6. (See text). The solid line is the theoretically expected curve of Eq. (11) with $a = 2$.

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.
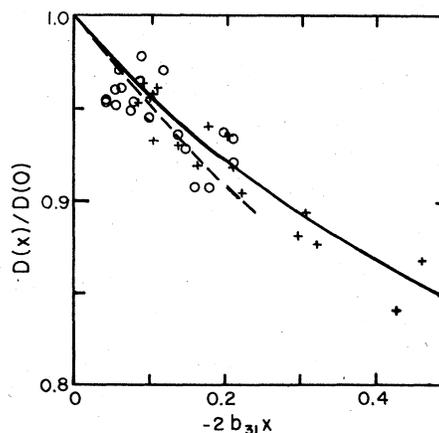
FIG. 8. Ratio of diffusivity of Au into Pb alloys to that of pure Pb (where x is the alloy concentration) as a function of $-2b_{31}x$. The solid line is the theoretical expression for Pb(Pd) alloys and the dashed line for Pb(Ag) alloys. (+) Pb(Pd) data, (○) Pb (Ag) data.
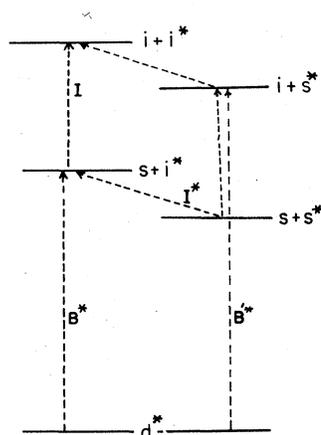
FIG. 9. Various two-particle states of two different impurities in lead. $d*$ is a substitutional dimer formed of the two. i is an interstitial impurity and s is a substitutional impurity. The asterisk denotes the tracer impurity.

To further interpret measurements of b_{21} and b_{31} let us replace c_v/k_1 in Eq. (7) by its value calculated in Eq. (6). We find

$$b_{31} = -q_0^*(1-q_0)/k_3, \quad b_{21} = -2q_0^*(1-q_0^*)/k_6 .$$ (12)

Now from Fig. 9 showing the two particle states of the substitutional dimer and Eq. (2) we obtain $k_3 = \frac{1}{6}\exp(-B*/kT)$ and $k_6 = \frac{1}{3}\exp(-B/kT)$. In these expressions the 3 and 6 originate from orientations of an A-A substitutional dimer with a binding energy B or the six orientations of an A-B substitutional dimer with binding energy $B*$. We assumed, for a constant pressure process, the substitutional dimers to be oriented in the [100] direction. Assuming $B*$ is a Gibbs free energy $B* = H* - TS*$, etc.,

$$b_{31} = -6q_0^*(1-q_0)e^{-S*/k}e^{H*/kT} ,$$ (13)

$$b_{21} = -6q_0^*(1-q_0^*)e^{-S/k}e^{H/kT} .$$

Using the expressions in DCV for q_0 and q_0^* we can interpret C_1 as follows:

$$C_1 = \frac{-6(1-q_0)e^{-S*/k}}{1+e^{-I*/kT}+6e^{-Q*/kT}}$$ (14)

for b_{31} and the same expression for b_{21} with q_0 replaced by q_0^* and $S*$ by S. In the temperature

range of these experiments, C_1 is essentially temperature independent giving the results for S shown in Table I. The value of C_2 by the same method is predicted to be equal to $H* - I*$ or $H - I*$ respectively, and in this manner we can calculate the binding energies for the various substitutional dimers shown in Table I. It is observed that the binding energies are apparently independent of the type of impurity to within the accuracy of the measurement. If we further assume that this binding energy is the same for all substitutional dimers in lead, we can predict other self-de-enhancement results, again using q_0 values from DCV and the expression

$$\frac{b_{21}'}{b_{21}} = \frac{q_0'(1-q_0')e^{S'-S'/k}}{q_0(1-q_0)} .$$ (15)

Since S does not appear to vary greatly for different types of atoms, we predict to within a factor of three that b_{21} for Ag, Pd, and Cu de-enhancement when diffusing in lead at 200°C to be 70, 1800, and 60, respectively. This is to be compared with the measured value of 1000 for Au. This value for Ag is in excellent agreement with the reported results of Cohen and Warburton.[15] We predict a very small de-enhancement by Cu on Cu diffusion in Pb but a very strong self-de-enhancement of Pd in lead.

It is easy to see from Fig. 9 that $B*$ for Ag*–Au substitutional dimers will equal $B'*$ for Au*–Ag substitutional dimers and using Eqs. (7) and (2) we find b_{31} (Ag*–Au) = b_{31}(Au*–Ag).

We can also theoretically estimate the value of a in Eq. (11) [See Eq. (7)],

$$a = \frac{4k_3q_0}{k_4q_0^*} = 2\frac{q_0}{q_0^*}\exp\frac{B-B*}{kT} \cong \frac{2q_0}{q_0^*} .$$ (16)

From Eq. (16) and values of q_0 from DCV we found the values of a (averaged over the range of temperatures of the diffusion measurements) shown in Table I. The data for Ag were analyzed using this value but the value of a, measured by the least-squared analysis, for the Pd alloys is in good agreement with this prediction. Hence, a for self-enhancement is equal to 2 because $q_0 = q_0^*$ and $B = B*$.

In the interpretation of this experiment we used DCV to determine equilibrium concentrations of

TABLE I. Various parameters determined from the de-enhancement measurements.

Impurity	Temperature range (°C)	a (theory)	a (expt)	S/k or $S*/k$	H or $H*$ (eV)
Pd	181–263	4.2	3.6±1.5	1.8±1.1	0.39±0.03
Ag	182–300	0.19	···	3.1±2.6	0.39±0.06
Au	137–238	2.0	···	3.0±0.8	0.40±0.02
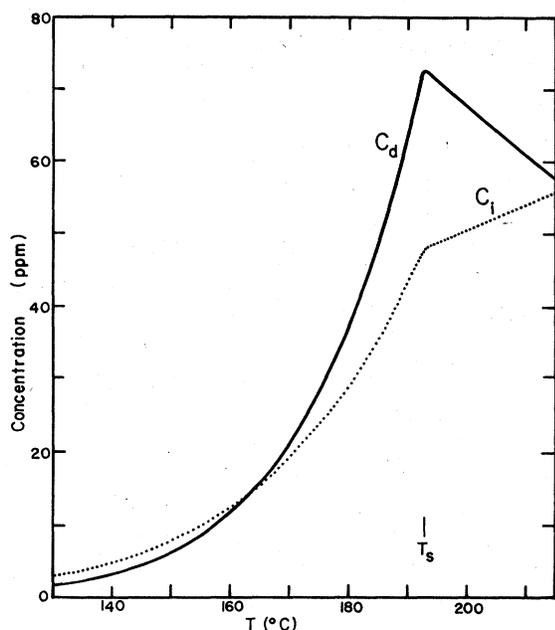
FIG. 10. Concentration of substitutional dimers (c_d) a and interstitials (c_i) of Au impurities in lead at equilibrium as a function of temperature with a total Au impurity concentration of 500 ppm. The remaining Au atoms are in substitutional states, T_s is the saturation-concentration temperature for 500 ppm Au in Pb.

interstitial impurities in lead. If we take those results at face value and determine the temperature dependence of $c_i(x)$ and $c_d(x)$ for gold in lead at equilibrium over the temperature range where x is near the saturation concentration we find the results in Fig. 10. The only unusual features in these functions in this figure appear at the saturation temperature T_s, where the concentration of dissolved defects begins to drop. We assumed in this calculation that as the temperature is lowered below T_s the gold precipitates in the lead to keep the free gold, in which category we included both the substitutional dimers and the singlet states of gold, at the saturation limit. We then observe a rapid decrease in the number of point defects which causes the resistivity to drop as the temperature drops below T_s.

We feel that the small effect in resistivity found in Pb(Au) alloys,[26] which appears at T_s, is not related to a change from singlet to substitutional dimer Au states as originally suggested but merely a reduced effect of precipitation. On quenching from the temperature $T_0 > T_s$ to room temperature the singlets and substitutional dimers find themselves in supersaturated states. At room temperature the interstitials diffuse rapidly enough to precipitate within short kinetic times. The substitutional and substitutional dimer impurity concentration, however, will remain for

relatively long periods of time at the levels characteristic of the quench temperature T_0. The resistivity measurements for Tl, Sn, Cd, Hg, and Ag in Pb in the Cohen et al. experiment according to DCV would be expected (and it was observed) to satisfy Matthiessen's rule because the interstitial concentration at T_0 was insignificant for these impurities. However, for Au impurities in Pb the interstitial fraction $q(x)$ from Eq. (5) with $a = 2$ and using q_0 from DCV was calculated to be 11.4% for all five alloys at the respective quench temperatures T_0. Upon quenching to room temperature we would assume that this interstitial fraction immediately precipitates. The unique conditions of the experiment,[26] in which the resistivity reassurements were extrapolated to zero quench times, are such as to expect the slowly diffusing substitutional and substitutional dimer concentrations to remain constant, characteristic of the quench temperature T_0. Under these assumptions the bridge voltage takes the form

$$\Delta V = xA\{1 - f[1 - \gamma(T)/\gamma(T_0)] - \rho_1(T)/\rho_1(T_0)\} , \quad (17)$$

where A is a normalization constant, $f = q(x)\rho_i/\rho_{av}$(impurity), $\gamma(T)$ is the precipitate resistivity, $\rho_1(T)$ is the pure Pb resistivity, and ρ_i is the interstitial resistivity per Au atom. The form of $\gamma(T)$ should be similar to the resistivity curves as shown in Ref. 22 and Fig. 1. A fitting function that is not an especially good approximation to the precipitate resistivity but which has most of the important features is given by

$$\gamma(T) = \rho_0/(e^{w(T_c - T)} + 1) . \quad (18)$$

The curve is nearly flat except over a relatively small temperature interval $T_{high} - T_{low} = 4/w$, centered at T_c where it increases from about zero to ρ_0 with increasing temperature. The resistivity data of Cohen et al. for 90-, 150-, 200-, 300-, and 350-ppm Au in Pb were simultaneously fit to Eqs. (17) and (18). The fit for f [which, it should be noted, was very insensitive to the form of Eq. (18)] was found to have a value of 0.21 ± 0.02 which is in good agreement with 0.11 ρ_i/ρ_{av}(impurity) from the model. The temperature T_{high} at the knee of the resistivity precipitation curve, defined as the temperature at the intersection of the line $\gamma = \rho_0$ and the line that is tangent to $\gamma(T)$ at $T = T_c(x)$, was found to be in excellent agreement with the precipitation temperatures. We found

$$T_{high} \equiv T_c(x) + 2/w = T_s \pm 2.3°C.$$

We conclude that although substitutional dimers of order greater than two, Au_3, Au_4, ..., can be introduced to explain the resistivity and diffusivity data for Au in Pb, they are not necessary and all

the data, at least to this point in time, can adequately be explained in terms of interstitial, substitutional, (interstitial-vacancy pairs), and impurity doublets.

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