

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  $c_0/k_1$  in Eq. (7) by its value calculated in Eq. (6). We find

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

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.,

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

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

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

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

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

$$\frac{b'_{21}}{b_{21}} = \frac{q'_0(1 - q'_0) e^{S - S'/k}}{q_0(1 - q_0)}. \quad (15)$$

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.<sup>15</sup> 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)],

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

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

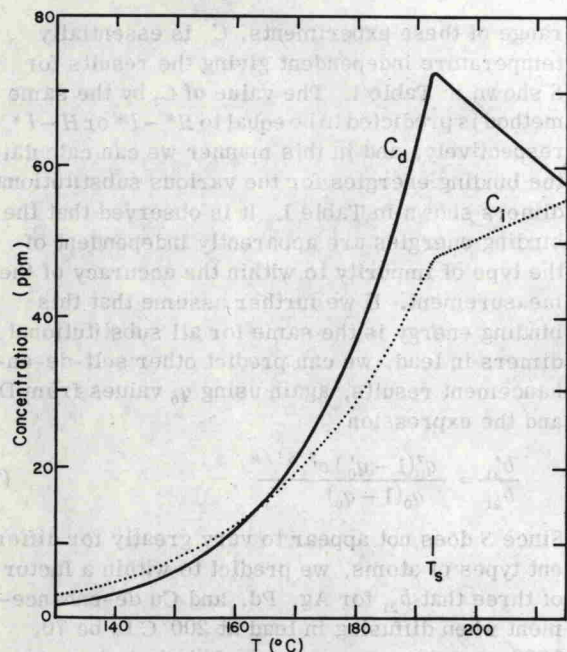


FIG. 10. Concentration of substitutional dimers ( $c_d$ ) and interstitials ( $c_i$ ) of Au impurities in lead at equilibrium as a function of temperature with a total Au impurity concentration of 500 ppm. The remaining Au atoms are in substitutional states,  $T_s$  is the saturation-concentration temperature 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,<sup>26</sup> 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,<sup>26</sup> in which the resistivity measurements 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,  $f = q(x)\rho_i/\rho_{av}(\text{impurity})$ ,  $\gamma(T)$  is the precipitate resistivity,  $\rho_1(T)$  is the pure Pb resistivity, and  $\rho_i$  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  $T_{\text{high}} - T_{\text{low}} = 4/w$ , centered at  $T_c$  where it increases from about zero to  $\rho_0$  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  $0.21 \pm 0.02$  which is in good agreement with  $0.11 \rho_i/\rho_{av}(\text{impurity})$  from the model. The temperature  $T_{\text{high}}$  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

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

We conclude that although substitutional dimers of order greater than two,  $\text{Au}_3, \text{Au}_4, \dots$ , can be introduced to explain the resistivity and diffusivity data for Au in Pb, they are not necessary and all