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

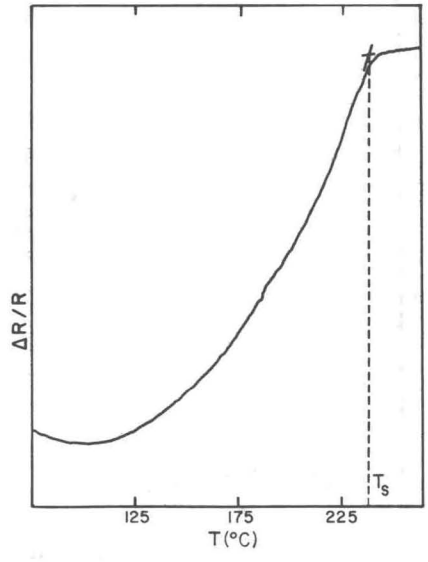

FIG. 1. Impurity resistance of 289-ppm Pd in Pb as a function of temperature. T_s is the temperature at which Pb is saturated with 289 ppm Pd.

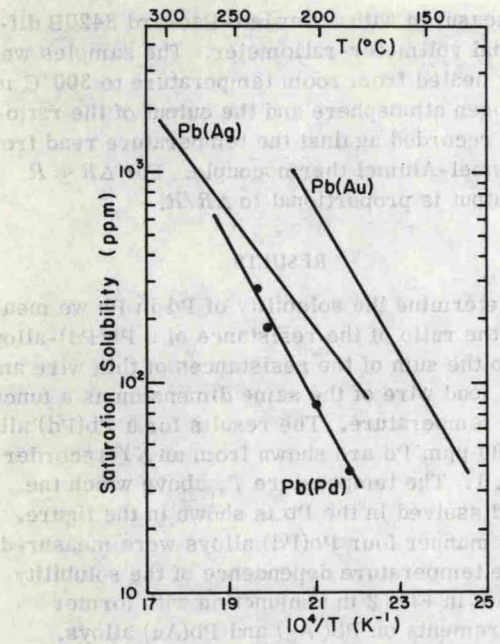

FIG. 2. Saturation solubility in atomic parts per million (ppm) of Pd, Ag, and Au in Pb as a function of temperature.

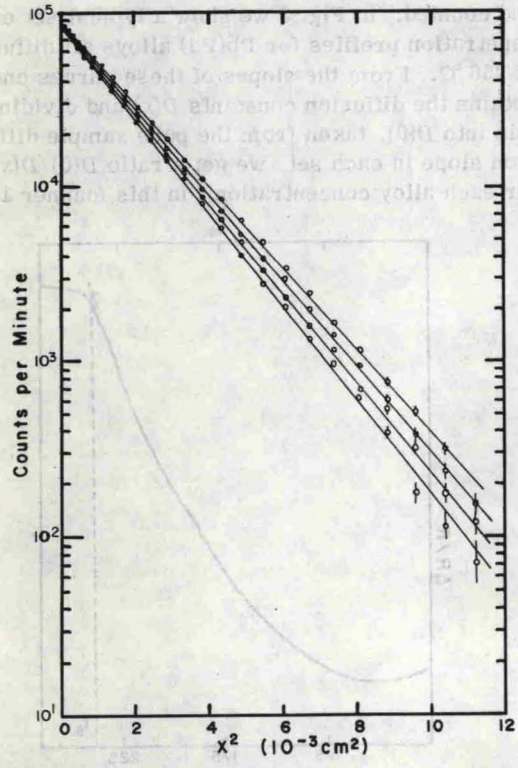

FIG. 3. Penetration profiles for Pb(Pd) alloys annealed at 256 °C for 590 sec. The curves starting from the top correspond to alloys containing 0, 87, 187, and 269 ppm Pd.

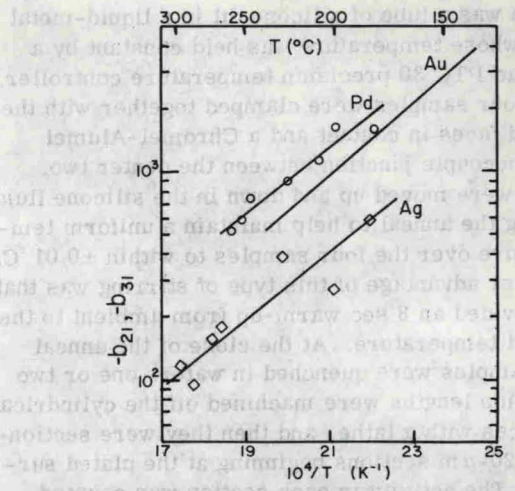

FIG. 4. Linear de-enhancement coefficient for the de-enhancement of Au diffusing in Pb alloyed with Pd, Au, and Ag. The measurements with Pd (○) and Ag (□) are reported herein and the Au results are taken from our analysis of data in Ref. 6.

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