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Diffusion of Sn in Pb to 30 kbar[†]

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The diffusion of ^{113}Sn in Pb was measured up to a pressure of 29 kbar with the following results: activation energy 1.03 ± 0.03 eV/atom, activation volume $\Delta V = 9.7 \pm 0.5$ cm^3/mole, $D_0 = 0.41 \pm 0.26$ cm^2/sec at the melting point at atmospheric pressure. The results are discussed in relation to lead self-diffusion and the anomalous diffusers in lead.

I. INTRODUCTION

Over the past several years, this laboratory has examined the effects of pressure on the diffusivity of a number of elements in pure lead.[1-7] All of these elements were chosen because of their relatively rapid diffusivity and low solubility in lead. All were found to respond to pressure with an activation volume considerably smaller than that for lead self-diffusion.[8] It was felt that this indicated some admixture of mechanisms with at least some of the diffusion processes taking place via jumping of interstitial atoms which would have a small response to pressure. All these experiments yielded relatively small activation volumes varying from 0.04 to 0.51 atomic volumes of Pb. This would indicate a significant variance in the predominant diffusion mechanism for these impurities in Pb.

Of all of these tracers in Pb there may be some fraction existing in interstitial positions which strongly dominates the diffusivities. It would be interesting to compare these results with those for a defect which should occupy only substitutional sites. Tin was chosen as a most probable candidate. It diffuses in Pb almost as sluggishly as with lead self-diffusion,[9] and is highly soluble,[10] all characteristic of a substitutional impurity. Thus, this experiment was undertaken to compare the pressure effect on the diffusivity of Sn in Pb to that of the "fast" diffusers in Pb.

II. EXPERIMENTAL DETAILS

These experiments were carried out in the same manner and in the same press as for the Zn in Pb work[7] with the following exceptions. No diffusion measurements were made for pressures above 30 kbar nor for temperatures above 450° C. The pressure measurements were limited because of the increasingly slow diffusivity and the temperature was limited because the pressure transmitting fluid carbonized and solidified at higher temperatures (for these long anneal times) thus distorting the Pb samples. We therefore increased the size of the hydrostatic pressure cell by using anvils made from shock-resistant tool steel whose square faces were 3.2 cm on an edge. The pyrophyllite cube was 3.8 cm on an edge and the liquid was enclosed by a 0.13-mm wall 8.8-mm-o.d. ×3.8-cm-long Inconel tube. The diffusion samples were single-crystal cylinders of Pb, 7-mm in diameter and 4-mm long, cemented with Sauereisen to the end of a steel cylinder 9 mm long with a central hole through which the thermocouple leads passed to a junction pressed into the end of the Pb cylinder. The exposed end of the lead was cut with a microtome just prior to electroplating with ^{113}Sn from a SnCl$_2$ bath. The Sn had a specific activity of 20 Ci/g and about 200 000 counts/min were plated. Annealing, sectioning, and counting techniques were the same as in Ref. 7.

Because of the change in the dimensions and geometry of the cell it was necessary to recalibrate the pressure versus load for this system. This was done by measuring the resistance of a Manganin coil versus the load in a cell containing Hg

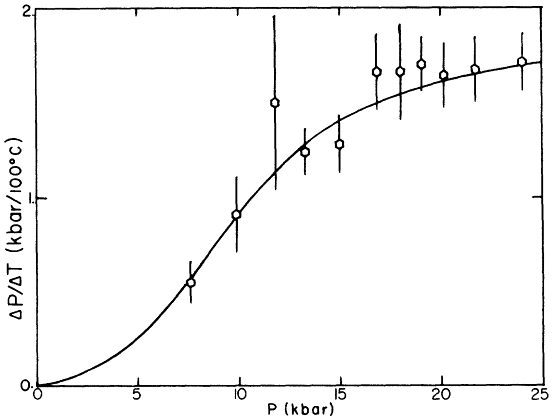

FIG. 1. Pressure increase upon heating an internal cell in a cubic multianvil press as a function of the pressure at ambient temperature. These results are for the cell described in the experimental section of this paper.

and Bi.[11] The melting of the Hg and the Bi I-II phase change were noted and used to calibrate the Manganin coil. In order to determine the pressure increase upon internal heating of the cell a sample was built containing a Bi and Pb sample with a differential thermocouple between them. The cell was heated noting the temperature along the melting curve of Bi and thus determining the pressure at these elevated temperatures and the increase of pressure with heating.[12] All the calibration and diffusion cells contained the same amount of liquid which was adjusted by placing the appropriate size lead disk in the bottom of the cell. This was necessary to make the calibration appropriate for the diffusion runs. The results of this calibration are shown in Fig. 1 where we have plotted the pressure increase upon heating as a function of the initial pressure measured at ambient temperature.

III. RESULTS

A typical diffusion profile is shown in Fig. 2. The profiles were Arrhenius (even though there was considerable Sn still on the surface at the close of the anneal) provided the plated surface was properly rinsed and wiped following electroplating. We also noted some curvature in the penetration profiles if the initial amount of Sn on the surface was increased. These could not be solubility effects for we were still far below the solubility limit. Neither could they arise from oxidation of the Sn during the diffusion anneal for then we would have observed effects as discussed in our article on Zn diffusion in Pb.[13] We suspect the problem was in not plating pure-Sn metal from the electroplating solution. We learned, however, to avoid the problem by keeping the total amount of Sn low, and thoroughly cleaning the electroplated surface.

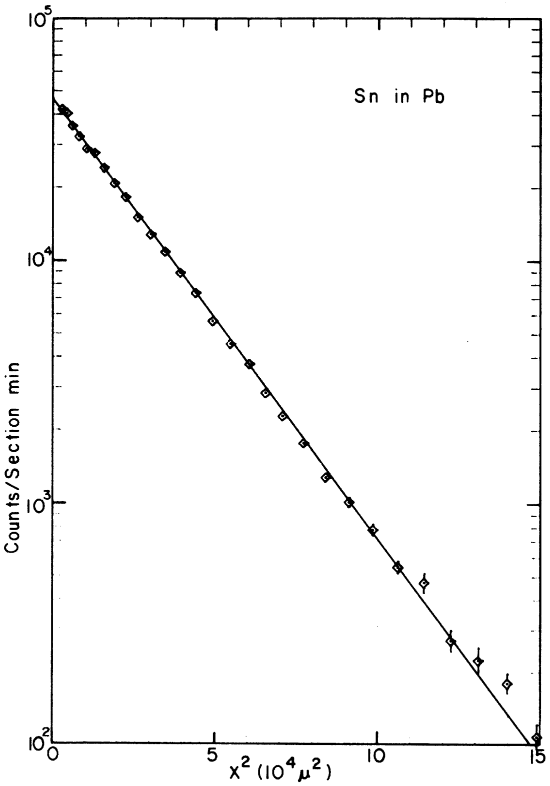

FIG. 2. Penetration profile of ^{113}Sn diffused into Pb for 13 h at 425 °C and 19.7 kbar.

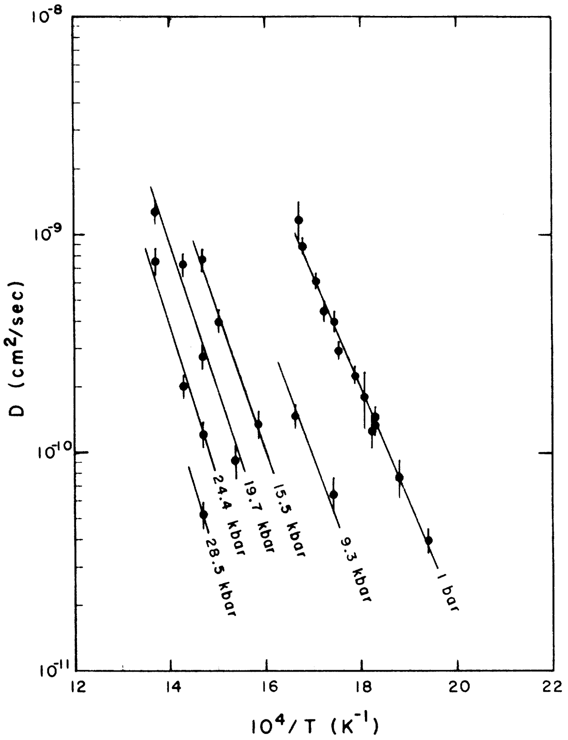

FIG. 3. Diffusion constant of Sn in Pb vs reciprocal temperature along selected isobars. The lines are the computer fit to the data.

The atmospheric-pressure results were all higher than those of Seith and Laird but had the same slope. (See Fig. 3.) All the results were analyzed by the method described previously.[2] Figure 3 shows both the experimental values of $D(P, T)$ and

TABLE I. Parameters determined from the measured diffusion of Sn in Pb. All evaluated at $T = 600\,°K$ and $P = 0$ kbar where $V_0 = 18.796$ cm^3/mol.

D_0	0.41	$\pm$ 0.26 cm^2/mol
ΔH	1.03	$\pm$ 0.03 eV/atom
$\Delta V/V_0$	0.517	$\pm$ 0.025
$\partial(\Delta V/V_0)/\partial P$	6.9	$\pm 2.6 \times 10^{-3}$ kbar^{-1}
$\partial(\Delta V/V_0)/\partial T$	-5.4	$\pm 3.1 \times 10^{-4}$ °K^{-1}
$\Delta C_p/R$	-4.1	$\pm$ 2.7

the computer-fitted diffusion isobars along the pressures for which data were taken. The diffusion parameters from the computer fit are given in Table I.

IV. DISCUSSION AND CONCLUSIONS

The calibration of $\Delta P/\Delta T$ is what one would expect in this large cell, for at the lower pressures the gaskets are not well formed, and thus as we internally heat the cell the internal expansion is relaxed by giving way of the gasket material. In fact heating at these low pressures often resulted in "blow outs," that is, a sudden relaxation in the gasket.

The activation energy of 1.03 ± 0.03 eV is between that of Pb self-diffusion 1.11 eV and Hg diffusion in Pb 1.000 eV, and could easily be in the range of vacancy-controlled diffusion of a substitutional impurity. However, the activation volume $[(0.52 \pm 0.03)V_0]$ is much more characteristic of the anomalous diffuser Hg $[0.52 \pm 0.01)V_0]$,[14] than of the self-diffusion result $[(0.71 \pm 0.02)V_0]$.[8] This indicates that even in the case of Sn diffusion in Pb we likely have more than just a well-behaved substitutional impurity. The contribution to the activation volume from the equilibrium concentration of vacancies should be nearly 0.5 V_0, leaving nearly zero pressure effect on the jumping of Sn into the vacancy, if the diffusion is completely by substitutional defects. This seems unrealistic. It is also to be noted that the Sn activation volume measurement lies on the curve of activation volume versus r^{++} proposed in a former paper.[7] This is still a most curious result but probably indicates the Sn-diffusion mechanism is more like an extention of that of the other impurities than like that of Pb self-diffusion.

The earlier atmospheric-pressure results[9] must be slightly low for they are not only inconsistent with our atmospheric pressure work but would not fit in well with the pressure data. There might be an effect due to the larger concentration of Sn used by the earlier workers.

If we assume that the low-activation volume is due to the presence of some interstitial Sn solubility in Pb we could inquire as to what fraction of the Sn must be interstitial. Using the equations for ΔH, ΔV, and D at the melting point and atmospheric pressure versus the fraction of the solute in interstitial (q) and interstitial-vacancy pair (p) states,[6] we find $q = 5.4 \pm 1.4 \times 10^{-5}$ and $p = 1.0 \pm 2.5 \times 10^{-4}$. Thus we need only 0.005% of the Sn atoms to be in interstitial states to get the low-activation volume measured and a diffusion constant about 2.4 times that of Pb self-diffusion at the melting point.

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