

## Brief Reports

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### Comment on solute diffusion in Pb: The size effect

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Recently published data for diffusion in Pb of Pt, Co, and Sn, as well as an earlier result for Sb, are considered in the light of atomic size-effect correlations. It is found that the data for all solutes conform to the size-effect description.

#### I. INTRODUCTION

In a recent study of the diffusion of Pt in Pb, Vanfleet<sup>1</sup> noted that there was some prior indication that Pt diffusion in Pb might be very slow. Consideration of a rather well obeyed empirical correlation between atom size and impurity diffusion in Pb would, on the other hand, have suggested quite the reverse, namely, that Pt diffusion in Pb should be very fast.<sup>2</sup> The latter observation was precisely the one which was made.

It is the purpose of this short note to show how the results of four heretofore unconsidered—in the light of the size-effect correlation—experimental investigations of impurity diffusion in Pb<sup>1,3-5</sup> fit the predictions of the size-effect correlation and to update the parameters characterizing the correlation, accordingly.

#### II. DISCUSSION

There have been a number of attempts made to correlate tracer diffusion parameters with atom size effects, notable among which was a publication by Swalin.<sup>6</sup> In general, however, these efforts have been largely unsuccessful<sup>7,8</sup> compared to results for formulations based essentially on electrostatic charge effects<sup>7,9</sup>; one apparent exception, however, concerns a recent exposition<sup>2</sup> of systematic size effects in tracer diffusion in Pb,  $\alpha$ -Zr, and Cu. There it was found that the tracer diffusion coefficient  $D$ , at a given fraction of the melting temperature ( $\sim 0.6T_m$ ), could be related to the atomic radius ( $r$ ) of the tracer element<sup>10</sup> by an equation of the general form

$$\ln D = A \pm \exp(c - br). \quad (1)$$

For tracer diffusion in Pb, at 360 K, a least-squares-fitted equation corresponding to Eq. (1) was,<sup>2</sup> for  $r > 1.35 \text{ \AA}$ ,

$$\log_{10} D = -17.77 \pm 1.81 + \exp[7.91 \pm 2.07 - (4.04 \pm 1.61)r], \quad (2)$$

with  $D$  expressed in units of  $\text{cm}^2\text{s}^{-1}$ .

Since, for tracer diffusion in Pb, there is a relatively good correlation of the type deduced by Zener<sup>11</sup> between the activation enthalpy  $h$  and the pre-exponential factor  $D_0$  in the usual Arrhenius equation describing the temperature dependence of  $D$ ,

$$D = D_0 \exp(-h/kT), \quad (3)$$

it followed that  $D_0$  and  $h$  could be expressed in terms of  $r$  as the only variable. The correlation between  $D_0$  and  $h$  was<sup>2</sup>

$$D_0 = 2.0 \times 10^{-4} \exp(0.345h) \quad (4)$$

in  $\text{cm}^2 \text{s}^{-1}$  and between  $h$  and  $r$  the correlation was  $h = 1.336 \pm 0.173 - \exp[5.51 \pm 1.32 - (4.04 \pm 1.61)r]$  (5)

in eV. Hereafter, the units of  $D$  (and  $D_0$ ),  $h$ , and  $r$  are  $\text{cm}^2 \text{s}^{-1}$ , eV, and  $\text{\AA}$ , respectively.

Equation (2) and, accordingly, Eq. (5) describe the experimental data well except at the smallest values of  $r$  where both  $D$  and  $h$  appear to cut off toward limiting values.

TABLE I. Experimental and calculated  $D$  and  $h$  values for solute diffusion in Pb.

Solute	Metallic radius $r$ ( $\text{\AA}$ )	$\log_{10} D$ (360 K) ( $\text{cm}^2\text{s}^{-1}$ )		$h$ (eV)	
		Expt.	Eq. (2)	Expt.	Eq. (5)
Sn	1.584	-14.4	-13.2	0.953	0.925
Sb	1.590	-14.0	-13.4	0.963	0.934
Pt	1.387	-8.09	-7.73	0.369	0.425

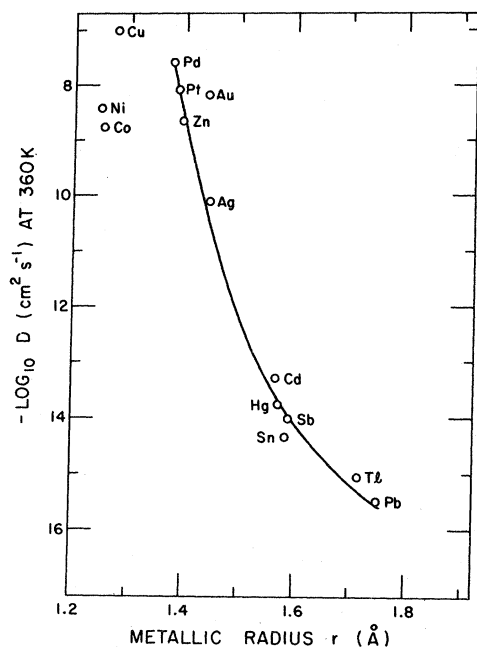


FIG. 1. Logarithm of the solute diffusion coefficient in Pb at 360 K (extrapolated from higher-temperature diffusion data) as a function of the metallic radius of the solute atom. The full line is a best-fit exponential—see Eq. (6) in text.

Since the original  $D/r$  correlation for Pb,  $\alpha$ -Zr, and Cu was made, studies of the temperature dependence of diffusion in Pb have been made for three further elements, Pt, Sn, and Co.<sup>1,3,5</sup> These results, along with previously published, but hitherto unconsidered, data for Sb diffusion in Pb<sup>4</sup> will now be considered within the framework of size effects.

Insofar as can be judged, the diffusion data for Pt, Co, and Sb diffusion in Pb exhibit linear Arrhenius plots of  $\log D$  vs  $1/T$  over the range of measurements; for Sn, on the other hand, there appears to be a tendency for the temperature dependence of  $D$  to increase somewhat at the highest temperatures. For the purpose of examining the  $D/r$  correlation at 360 K the  $D$  values for Pt, Co, and Sb have therefore been obtained by extrapolation of the experimental data via the  $h$  and  $D_0$  parameters presented in these studies,<sup>1,4,5</sup> while the corresponding  $D$  value for Sn in Pb was estimated from an extrapolated linear fit of the lower-temperature experimental data from that work.<sup>3</sup>

Although the data for Sn, Sb, and Pt conform fairly well to Eqs. (2) and (5)—see Table I—improved least-squares fits were obtained when the additional data were included in a reanalysis of the results.<sup>12</sup> The revised equations are

TABLE II. Experimental and calculated  $h$  values for solute diffusion in Pb.

Solute	Metallic radius (Å)	$h$ (eV)		$\frac{h(\text{expt}) - h(\text{Eq. 7})}{h(\text{expt})}$ %
		Expt.	Eq. (7)	
Pd	1.376	0.367	0.383	-4
Pt	1.387	0.438	0.435	+1
Zn	1.394	0.495	0.467	+6
Au	1.442	0.386	0.649	-68
Ag	1.445	0.629	0.659	-5
Cd	1.568	0.920	0.934	-2
Hg	1.573	0.985	0.941	+4
Sn	1.584	0.953 <sup>a</sup>	0.957	0
Sb	1.590	0.963	0.964	0
Tl	1.716	1.05	1.07	-2
(Pb)	1.750	1.11	1.09	+2

<sup>a</sup> The value of  $h$  (expt) for Sn diffusion in Pb does not take into account the two highest-temperature data—see Fig. 3 of Ref. 3 and comment in Sec. 2, here.

$$\log_{10} D(360 \text{ K}) = -16.55 \pm 0.59$$

$$+ \exp[10.12 \pm 1.15 - (5.76 \pm 0.87)r]$$

(6)

and

$$h = 1.17 \pm 0.05 - \exp[8.38 \pm 1.18 - (6.27 \pm 0.89)r]. \quad (7)$$

Figure 1 shows how the experimental diffusion data conform to Eq. (6) and Table II compares the experimental activation energies with values calculated from Eq. (7). In both cases, agreement between experimental and calculated values is, with the exception of the results for Co, Cu, Ni, and Au, good. It is apparent that the data for Co, Cu, and Ni fall outside the range of the smooth  $D/r$  correlation and so, as before,<sup>2</sup> they were not included in the analyses. The Au data were also excluded from the fitting procedure on the grounds that while their inclusion did not radically alter the constants shown in Eqs. (6) and (7), it was sufficient to detract considerably from the quality of the fits shown in Fig. 1 and Table II.

In contrast to the earlier work, the constants for Eq. (7) were determined directly from a least-squares fit of the experimental  $h$  data without proceeding via the agency of a fitted  $D_0$  vs  $h$  correlation. The quoted uncertainties on the parameters in Eqs. (6) and (7) represent one standard deviation; for other comments regarding the uncertainties to be associated with the data, the reader is referred to Ref. 2.

In summary, additional solute-diffusion data for diffusion in Pb have been found to conform well to a previously developed atom size-effect description.

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- <sup>9</sup>D. Lazarus, *Phys. Rev.* 93, 973 (1954).
- <sup>10</sup>E. Teatum, K. Gschneider, and J. Waber, Report No. LA-2345, U.S. Dept. of Commerce, Washington, D.C., 1960 (unpublished). See also W. B. Pearson, *The Crystal Chemistry and Physics of Metals and Alloys* (Wiley, New York, 1972), Chap. 4.
- <sup>11</sup>C. Zener, *J. Appl. Phys.* 22, 372 (1951).
- <sup>12</sup>It has been pointed out to the author that the published  $D_0$  and  $h$  values for Na diffusion in Pb do not agree with the results shown in Fig. 3 of that work [C. W. Owens and D. Turnbull, *J. Appl. Phys.* 43, 3933 (1972)]. In view of this uncertainty the data for Na diffusion in Pb (included in the size-effect analyses in Ref. 2) have been excluded from this study.