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Diffusion of Pb and Hg in Dilute Pb:Hg Alloys

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The diffusion of Pb and Hg was measured in Pb : Hg alloys of up to 8-at.% mercury between 200 and 300 °C by the serial-sectioning technique. The diffusion of mercury in pure lead is well described by $D_{\mathrm{Hg}} = D_0 e^{(-H_{\mathrm{Hg}}/RT)}$, where $D_0 = 1.05 \pm 0.24$ cm^2/sec and $H_{\mathrm{Hg}} = 22.7 \pm 0.2$ kcal/mole, and is 15–20 times faster than the lead self-diffusion. The diffusivities of both lead and mercury are enhanced by increasing the mercury content of the alloys. This is incompatible with an interstitial mechanism. The enhancement coefficients, measured at four temperatures, are very small and lie close to the minimum allowed by a vacancy mechanism. The predictions of both vacancy and interstitial-vacancy pair models are reviewed and compared to the present data. This shows that neither model in its present form gives a fully satisfactory description of this system's diffusion behavior and so a possible extension of the interstitial-vacancy pair model is suggested.

I. INTRODUCTION

Studies of impurity-diffusion behavior in lead have produced several advances in our understanding of the factors which affect defect formation in metals. The study of gold diffusion in lead by Seith and Keil[1] was one of the first observations of ultrafast impurity diffusion. Later it was shown that all the noble metals exhibit this behavior and in fact diffuse by an interstitial mechanism.[1–4] This led Anthony and Turnbull[5] to consider what factors might stabilize an impurity atom in an interstitial site. These factors include the screening of the impurity's charge by the large number of conduction electrons in a polyvalent host, correlation binding between the impurity's *d* electrons and the host-ion cores, and an unusually large interstitial site resulting from lead's small core size. Miller[6,7] therefore studied the behavior of cadmium in lead in an attempt to determine whether an increase in impurity size and valence would decrease the likelihood of forming interstitial defects as predicted. This indeed proved to be the case, for he concluded that an interstitial cadmium could only be stabilized in association with a vacancy and that these interstitial-vacancy pairs were responsible for the diffusion behavior he observed.

Further information is still needed, however, to fully sort out the influences of the various factors, and we considered it advantageous to study the behavior of another group-II metal, either zinc or mercury, which would have the same valence as cadmium but a different atomic size. Experimentally, lead-mercury makes the better system since mercury has a much higher solid solubility in lead, which is of great utility in studying enhancement effects. Also, the mercury tracer wets a fairly clean lead surface, whereas zinc forms such a stable oxide that it causes serious surface holdup problems. Therefore, with the object of further elucidating the factors influencing defect formation in metals, we have made a detailed study of the diffusion behavior of lead and mercury in Pb: Hg alloys of up to 8-at.% mercury over a temperature range 200–300 °C.

II. EXPERIMENTAL TECHNIQUES

All measurements were done on single-crystal specimens grown, using Cominco 99.9999%-pure lead and triple-distilled mercury, from the melt in high-purity graphite boats by a modified Bridgman technique. These $\frac{1}{2}$-in.-diam crystals were sliced into samples 0.2 in. thick using a Servomet sparkcutter. The ends of the crystals, which would have a mercury gradient, were not used. Samples which produced results substantially out of line with their neighbors in the enhancement experiments were further checked with an electron microprobe to independently ascertain their compositions and check their homogeneity.

Prior to plating, samples were faced-off on a sliding-blade microtome, finishing with 2-μ cuts to leave a clean, minimally damaged surface. No recrystallization was ever observed to result from this procedure. The clean face was immediately plated with the appropriate tracer, usually within $\frac{1}{2}$ min, and no problems with surface holdup were encountered. The tracers used were Pb^{210}, which was plated from a dilute cyanide bath described elsewhere,[8] and Hg^{203}, which was plated from a bath consisting of about 5 mCi of Hg^{203}, supplied as $Hg(NO_3)_2$, in 20-ml 0.5-*N* HNO_3. Plating currents used were a few mA/cm^2. The samples were then potted in Sylgard No. 185 silicone rubber primarily to prevent mercury loss from the alloys by evaporation during the diffusion anneals. The rubber surrounding several of the Hg^{203} diffusion samples was checked for radioactivity after the anneal and was found to be inactive, an indication that the rubber was effectively encapsulating the alloys. The secondary benefit of this process was protection of the samples against oxidation during the anneals.

Care was taken to ensure that the samples in a given enhancement run all experienced an identical thermal history during the diffusion anneal. To this end, they were tightly packed in order of increasing mercury concentration into snug-fitting aluminum canisters with a $\frac{1}{4}$-in.-thick wall by $1\frac{1}{4}$-in. diam. and placed in furnaces whose constant-temperature zone was at least 1 in. longer than the canister. The temperature difference between the most separated samples in the canister is estimated to be less than $\frac{1}{10}$ °C. Such a difference would cause less than 2% of the typical difference in diffusion rates observed between these samples, which was always greater than a factor of 3. The error in enhancement factors from temperature differentials is thus expected to be negligible compared to that from other sources. Typically, however, mean annealing temperatures are known only to within about 1 °C due to long-term fluctuations.

After being annealed, the samples' diameters were turned down on a lathe at least 0.030 in. to exclude possible surface-diffusion effects and then sectioned on the microtome, the sections being weighed on a precision torsion balance with an accuracy of 0.02 mg. The sections containing Pb^{210} were then dissolved in a solution of 65% acetic acid–35% H_2O_2 prior to counting their activities since the Pb^{210} γ ray at 0.047 MeV is heavily absorbed in the sections. Since it is also absorbed by the solution and by the polystyrene counting tubes, the acid was dispensed from a metering syringe and a layer of Dow-Corning No. 200 silicone fluid with 10^5-cS viscosity floated over the solution in the tubes to prevent splashing and to standardize the counting geometry as much as possible. The counting was done in an automatic γ-ray counter with the window set from 0.240 to 0.340 MeV for Hg^{203} and from 0.035 to 0.059 MeV for the Pb^{210}.

Sample thicknesses were determined from their weight, diameter, and density in the usual way. The density of the alloys as a function of mercury concentration was calculated using the formula

$$\rho(\chi) = 11.3367 \pm 0.0022 + (0.01957 \pm 0.00074)\chi, \quad (1)$$

where ρ is in g/cm^3 and χ is the mercury concentration in atomic percent.[9] All the penetration plots were strictly Gaussian except at the deepest penetrations where "tails," possibly associated with faster diffusion along dislocations or with remnants of surface contamination, were occasionally observed. Such points were always excluded in fitting the data. Diffusion coefficients were then determined from a straight-line least-squares fit to values of ln (specific activity) versus penetration squared. All fitting was done by a matrix technique as suggested by Wolberg,[10] and the standard deviations were simultaneously obtained from the covariance matrix and depend only on the estimated errors in the input data.

Further details of the experimental technique may be obtained in Ref. 11.

III. EXPERIMENTAL RESULTS

Diffusion coefficients as a function of temperature are presented in Table I for four systems:

TABLE I. Diffusion coefficients and standard errors for diffusion of lead and mercury in pure lead and in two Pb : Hg alloys.

System	T (°C)	D (cm^2/sec)	σD(cm^2/sec)	Source
Pb^{210} in				
pure lead	294.6 ± 0.5	0.1233×10^{-9}	0.97×10^{-12}	enhancement
	274.1 ± 1.0	0.5541×10^{-10}	0.22×10^{-12}	enhancement
	251.8 ± 1.0	0.1924×10^{-10}	0.13×10^{-12}	enhancement
	225.5 ± 0.5	0.5375×10^{-11}	0.65×10^{-13}	enhancement
	214.0 ± 0.7	0.349×10^{-11}	0.32×10^{-13}	one couple
Pb^{210} in				
alloy *G*	294.6 ± 0.5	0.1599×10^{-9}	0.92×10^{-12}	enhancement
(~ 1-at.% Hg)	274.1 ± 1.0	0.7154×10^{-10}	0.32×10^{-12}	enhancement
	251.8 ± 1.0	0.2503×10^{-10}	0.38×10^{-12}	enhancement
	225.5 ± 0.5	0.7123×10^{-11}	0.30×10^{-13}	enhancement
	214.0 ± 0.7	0.422×10^{-11}	0.35×10^{-13}	one couple
Hg^{203} in				
pure lead	300.2 ± 1.0	0.240×10^{-8}	0.30×10^{-10}	enhancement
	272.0 ± 0.7	0.790×10^{-9}	0.15×10^{-10}	enhancement
	248.9 ± 0.4	0.320×10^{-9}	0.10×10^{-10}	enhancement
	224.0 ± 1.0	0.105×10^{-9}	0.13×10^{-11}	enhancement
	212.6 ± 1.5	0.640×10^{-10}	0.10×10^{-11}	one couple
	192.9 ± 0.7	0.240×10^{-10}	0.50×10^{-12}	enhancement
Hg^{203} in				
alloy *K*	294.0 ± 0.7	0.430×10^{-8}	0.45×10^{-10}	one couple
(~ 4-at.% Hg)	272.0 ± 0.7	0.180×10^{-8}	0.13×10^{-10}	enhancement
	248.9 ± 0.4	0.790×10^{-9}	0.50×10^{-11}	enhancement
	223.4 ± 0.8	0.270×10^{-9}	0.50×10^{-11}	one couple
	224.0 ± 1.0	0.280×10^{-9}	0.50×10^{-11}	enhancement
	212.6 ± 1.5	0.160×10^{-9}	0.10×10^{-11}	one couple
	173.9 ± 1.0	0.260×10^{-10}	0.50×10^{-12}	enhancement
	155.0 ± 0.8	0.840×10^{-11}	0.16×10^{-12}	enhancement

TABLE II. Compositions of alloys used in enhancement experiments, including nominal compositions and estimated errors used in curve fitting.

Name	Nominally (at.% Hg)	Composition (at.% Hg)	Error (at.% Hg)
A	0	0.000	0.001
B	$\frac{1}{8}$	0.130	0.010
C	$\frac{1}{4}$	0.255	0.010
D	$\frac{3}{8}$	0.385	0.010
E	$\frac{1}{2}$	0.512	0.020
F	$\frac{3}{4}$	0.751	0.020
G	1	1.000	0.020
H	1.5	1.500	0.020
I	2	1.984	0.020
J	3	3.000	0.020
K	4	4.001	0.020
L	7	7.062	0.030
M	8	8.001	0.030
NE	$\frac{1}{2}$	0.498	0.020
OI	2	2.004	0.020

Pb^{210} diffusing in pure lead and in a Pb–1-at.% Hg alloy and Hg^{203} diffusing in pure lead and in a Pb–4-at.% Hg alloy. The exact alloy compositions are listed in Table II. The experimental values are of two types: those determined from a single penetration profile and those determined from enhancement measurements. The latter are typically more accurate (as reflected in the standard deviations listed) and are thus weighted more heavily in the least-squares determination of the diffusion constants.

For all four systems, the data form quite straight lines on an Arrhenius plot, as shown in Fig. 1, and so are well represented by the usual form $D = D_0\, e^{-Q_D/RT}$. The values of the diffusion constants D_0 and Q_D were obtained from a least-squares fit of $\ln D$ vs $1/T$. These fitted lines are also indicated on Fig. 1 and the resultant values of the preexponential D_0's and heats of diffusion Q_D are presented in Table III. As an indication of the accuracy of the present work, we note that the values for the diffusion constants of Pb^{210}

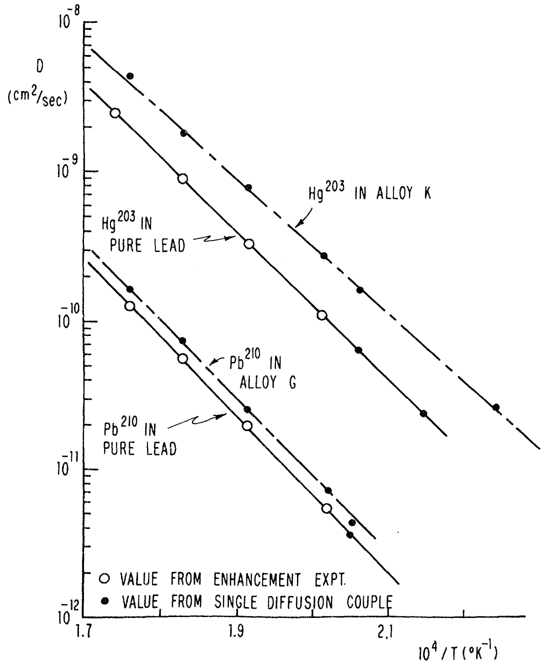

FIG. 1. Diffusivity of Hg^{203} and Pb^{210} tracers in pure lead and in two Pb : Hg alloys.

TABLE III. Diffusion constants for the diffusion of lead and mercury in pure lead and in two alloys.

System	D_0 (cm^2/sec)	Q_D (kcal/mole)	Range (°C)
Pb^{210} in pure lead	$0.88^{+0.60}_{-0.35}$	25.5 ± 0.5	214–295
Pb^{210} in alloy *G* (~ 1-at.% Hg)	$0.76^{+0.21}_{-0.14}$	25.1 ± 0.3	214–295
Hg^{203} in pure lead	$1.05^{+0.27}_{-0.21}$	22.7 ± 0.2	193–300
Hg^{203} in alloy *K* (~ 4-at.% Hg)	$0.79^{+0.17}_{-0.14}$	21.5 ± 0.2	155–295

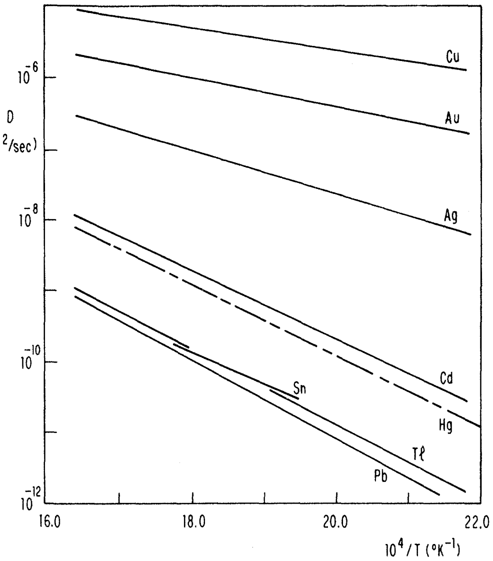

FIG. 2. Diffusivities of Cu, Au, Ag, Cd, Hg, Sn, Tl, and Pb in pure lead.

in pure lead agree within experimental error with the values quoted by Resing and Nachtrieb[12] and by Hudson and Hoffman,[13] and are identical with those of Miller[6] (see Table III). Curiously, even the results for the Hg^{203} diffusion in Pb–4-at.% Hg alloy are well represented by a single activation energy, though the enhancement studies show that at least one-half the diffusion is proceeding by higher-order processes which might be expected to have activation energies differing from that of the first-order process. The value of Q_D has, however, dropped about 1 kcal/mole from the pure-lead value and D_0 may have decreased a bit as well.

The diffusion of mercury in pure lead will be seen in better perspective when compared to the diffusion of other impurities in lead. This is done in Fig. 2, where curves for copper, silver, gold, cadmium, thallium, tin, and lead in lead are included. The corresponding diffusion constants are given and referenced in Table IV. First it is clear from Fig. 2 that mercury diffuses several orders of magnitude more slowly than any of the noble metals, which are presumed to diffuse mainly by an interstitial mechanism. A good summary of the experiments and thought leading to this latter conclusion is given in Ref. 15. Since, as is clear from Fig. 1, the mercury also enhances both its own and lead's diffusion, it cannot be diffusing by a purely interstitial mechanism. On the other hand, however, its diffusion rate *is* about 15 times faster than the self-diffusion rate and also much faster than the rates of thallium and tin in lead, which are expected to be diffusing by a vacancy mechanism.[6,12] This is quite different from the case of mercury in tin,[16] which diffuses at almost exactly the same rate as its host. Mercury's diffusion rate in lead is, in fact, most like that of cadmium, with an activation energy larger by only 1.5 kcal/mole, and this strongly suggests that mercury and cadmium may diffuse by similar mechanisms.

As we just noted in regard to Fig. 1, additions of mercury to lead definitely enhance the diffusion of both Pb^{210} and Hg^{203} tracers in these alloys. This effect was carefully studied in the present work both for its intrinsic interest and because, in the case of cadmium diffusion in lead, it provides a clear indication that the diffusion is not proceeding by a vacancy mechanism. While the enhancement of the lead self-diffusion was of primary interest, the enhancement of the mercury was also examined. The diffusion coefficients of both species were therefore measured as a function of mercury concentration on a series of alloys ranging between pure lead and either the solubility limit or 8-at.% mercury, whichever was lower. Measurements were made at about 225, 250, 275, and 300 °C. Since major interest focused on the linear enhancement terms, many more alloys of low concentration than high were used, the function of the latter being primarily to correct for higher-order effects. The actual concentrations of all alloys used are given in Table II. It should be repeated that the complete series of alloys used at any given temperature was annealed simultaneously, as described in the section on experimental technique.

The resultant diffusion coefficients, scaled by the value measured at zero concentration $D(0)$, could then be plotted as a function of the concentration χ. Typical graphs of the resultant enhancement curves, for lead and mercury diffusion, re-

TABLE IV. Diffusion constants for Cu, Ag, Au, Cd, Hg, Sn, Tl, and Pb in pure lead.

Tracer	Ref.	D_0 (cm^2/sec)	Q_D (kcal/mole)	Range (°C)[a]
Cu	2	7.9×10^{-3}	8.02 ± 0.40	220–mp
Ag	2	4.6×10^{-2}	14.44 ± 0.50	125–mp
Ag	1	7.5×10^{-2}	15.2	120–320
Au	1	1.03×10^{-1}	14.7	200–320
Au	3	8.7×10^{-3}	10.0	190–320
Au	4	4.1×10^{-3}	9.35	94–325
Cd	6	4.1×10^{-1}	21.23 ± 0.20	150–mp
Hg	b	$1.05\times10^{+0}$	22.7 ± 0.20	193–300
Sn	14	1.6×10^{-1}	23	245–285
Tl	12	5.1×10^{-1}	24.3 ± 0.20	206–323
Pb	12	$1.4\times10^{+0}$	26.1 ± 0.40	206–323
Pb	13	7.15×10^{-1}	24.8 ± 0.60	165–mp
Pb	6	8.9×10^{-1}	25.5 ± 0.30	150–mp
Pb	b	8.9×10^{-1}	25.5 ± 0.50	214–295

[a] Melting point is abbreviated mp.
[b] Value determined in this work.

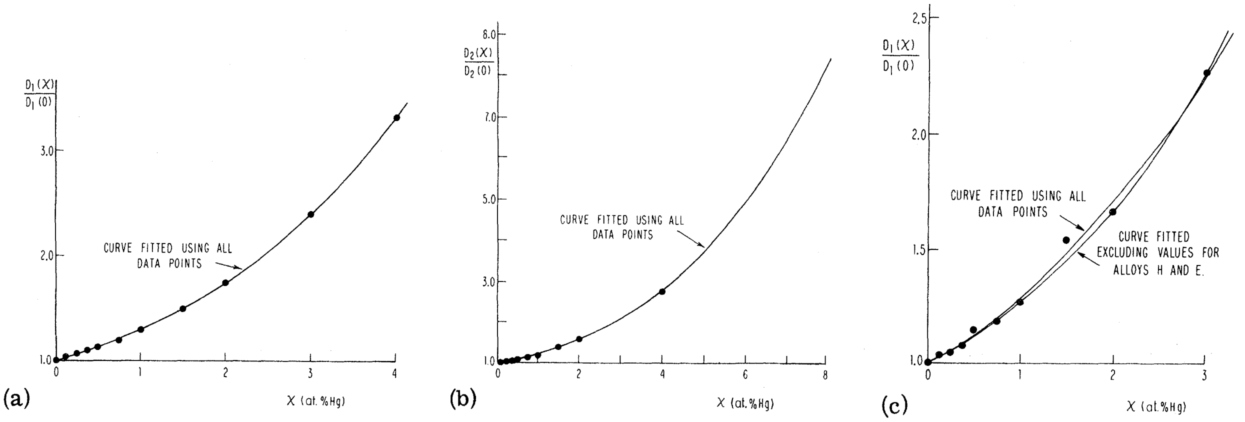

FIG. 3. (a) Enhancement of lead self-diffusion by additions of mercury at 274 °C. (b) Enhancement of mercury diffusion by additions of mercury at 224 °C. (c) Enhancement of lead self-diffusion by additions of mercury at 295 °C.

spectively, are shown in Figs. 3(a) and 3(b). The enhancement curves were then fitted, using the least-squares matrix technique mentioned earlier, with a third-degree polynomial of the form

$$D_i(\chi)/D_i(0) = A_i + b_{i1}\chi + b_{i2}\chi^2 + b_{i3}\chi^3, \qquad (2)$$

where $i = 1$ for lead and 2 for mercury. b_{i1} is the first enhancement coefficient, b_{i2} the second, etc. In Figs. 3(a) and 3(b) the fitted curves thus obtained have been drawn. The parameter t^2 was calculated in each case as an indication of the goodness of fit. Here $t^2 = S/k$, where S is the sum of the squared deviations of the points from the fitted curve and k equals the number of data points minus the number of fitting parameters, here equal to four. The function of k is to compensate the value of t^2 for improvements in fit which result purely from a decrease in number of points to be fit. If the value of t^2 indicated a poor fit, a search was made for experimentally bad points by the procedure of removing suspects, refitting, and comparing the new value of t^2 to the old. This process is shown in Fig. 3(c), where a fit to all points gave $t^2 = 3.4$. Only removing the point from alloy H improved matters much, giving $t^2 = 1.2$. After this the only point whose removal was significant was that from alloy E, giving a value of $t^2 = 0.63$, and the reported enhancement parameters. In the case of lead diffusion at 251.8 °C, nothing reduced t^2 much below about 1.8 and several such results were averaged to give the reported value of b_{11}. The values of the diffusion coefficients used in these three figures are given in Table V. It should also be noted that the term A_i in Eq. (2) is a correction for experimental error in the measured value of $D_i(0)$. The diffusivities used to calculate the heats of diffusion Q_D, reported earlier in this section, were thus $D_i(0)$ times A_i.

The enhancement coefficients obtained from these least-squares fits are presented in Tables VI and VII, including their standard errors, the exact temperatures of measurement, and the values of t^2 from the fits. Clearly, only the first enhancement coefficients, presented in Table VI, have much statistical significance. These two sets

TABLE V. Values of diffusion coefficients and errors used in Figs. 3(a), 3(b), and 3(c).

Alloy	Lead diffusivity at 275 °C (10^{-12} cm^2/sec)	Mercury diffusivity at 225 °C (10^{-11} cm^2/sec)	Lead diffusivity at 300 °C (10^{-11} cm^2/sec)
A	55.16 ± 0.21	10.54 ± 0.08	12.35 ± 0.10
B	57.63 ± 0.29	10.87 ± 0.09	12.88 ± 0.18
C	59.18 ± 0.21	11.06 ± 0.09	13.00 ± 0.13
D	60.81 ± 0.26	11.27 ± 0.09	13.30 ± 0.12
E		11.58 ± 0.09	14.24 ± 0.11
NE	62.34 ± 0.29		
F	65.71 ± 0.31	12.14 ± 0.10	14.77 ± 0.10
G	71.54 ± 0.32	12.71 ± 0.11	15.76 ± 0.10
H	82.33 ± 0.44	14.88 ± 0.12	19.07 ± 0.14
I		16.86 ± 0.13	20.47 ± 0.16
OI	96.24 ± 0.46		
J	131.6 ± 0.68	22.37 ± 0.18	28.08 ± 0.36
K	181.5 ± 1.14	29.23 ± 0.23	
M		103.39 ± 8.3	

TABLE VI. Linear enhancement coefficients for self-diffusion (b_{11}) and mercury diffusion (b_{21}) in Pb : Hg alloys.

T (°C)	b_{11}	t^2	T (°C)	b_{21}	t^2
294.6	22.1 ± 3.0	0.63	300.2	29.2 ± 4.3	1.28
274.1	23.2 ± 1.6	1.09	272.0	25.7 ± 3.3	2.10
251.8	27.2 ± 2.3	1.86	248.9	19.4 ± 3.2	0.74
225.5	28.2 ± 3.2	5.5	224.0	18.1 ± 2.9	1.51

TABLE VII. Second and third enhancement coefficients for self-diffusion (b_{12}, b_{13}) and mercury diffusion (b_{22}, b_{23}) in Pb : Hg alloys at four temperatures.

T (°C)	b_{12}	b_{13}	T (°C)	b_{22}	b_{23}
294.6	390 ± 290	9300 ± 7400	300.2	−740 ± 400	24800 ± 9500
274.1	490 ± 130	9000 ± 2700	272.0	−700 ± 150	6600 ± 1700
251.8	180 ± 95	14700 ± 1000	248.9	370 ± 150	3900 ± 1700
225.5	120 ± 150	22600 ± 1900	224.0	450 ± 190	5800 ± 3400

show different temperature dependence. The b_{21}'s, giving the mercury enhancement, form a monotonically increasing sequence with increasing temperature, while b_{11}'s, giving the lead enhancement, form a decreasing sequence. In Sec. IV we will compare both these sets of coefficients, as well as the values for the diffusivity, to the predictions of various models of diffusion mechanisms in order to see which, if any, can produce a consistent interpretation of the experimental data.

IV. COMPARISON WITH EXISTING MODELS OF DIFFUSION

Most of the existing models of diffusion mechanisms can quickly be shown to be incapable of interpreting the present experimental data. The interstitial mechanism, for example, cannot explain the observed enhancement, as was previously noted. Further, since this enhancement is typically of size

$$b_{11}(\mathrm{Hg/Pb}) \cong 1.5 D_{20}/D_{10} \tag{3}$$

(see Table IX), we can also discard the direct exchange and interstitialcy mechanisms, both of which would require the ratio to be unity, since in both mechanisms each impurity-atom jump is accompanied by a solvent atom jump. This is different from the case of cadmium in lead where the ratio was indeed nearly unity and the direct exchange mechanism could only be discarded on grounds of incompatibility with the isotope effect.[6] We are left then with only two likely models, diffusion by a vacancy mechanism and diffusion by interstitial-vacancy pairs. In the following paragraphs their properties will be summarized from the literature and then critically compared with the present experimental results.

A. Vacancy Mechanism

Diffusion by the vacancy mechanism is predominant in many common systems and has been the subject of much theoretical attention. In the standard treatment, introduced by Lidiard[17] and extended by others,[18–21] two assumptions are made. The first is that atoms, be they host or impurity, can move through the structure only by jumping into nearest-neighbor vacancies. The second is that the sole effect of an impurity atom in the structure is to modify the jump rates of local host atoms as shown in Fig. 4. From this figure we see that the impurity may diffuse faster or slower than the host, depending on the value of w_2/w_0, and that it is the deviations of jump rates w_1, w_3, and w_4 from the pure lattice value w_0 which cause enhancement effects in this model. While it appears that the four frequency ratios, w_1/w_0 through w_4/w_0, may be varied independently, this is not the case. In thermal equilibrium the population of impurities associated with vacancies is fixed by the energy of interaction between them, forcing w_3 and w_4 to be related in a way that maintains the population. Lidiard has shown the relationship to be[17]

$$w_4/w_3 = e^{-E_b/RT}, \tag{4}$$

where E_b is the energy of association of the pair. The three remaining independent frequency ratios are then usually taken to be w_2/w_1, w_4/w_0, and w_3/w_1.

The relation between this association energy and the impurity-diffusion behavior has been treated via an electrostatic theory introduced by Lazarus[22] and extended by LeClaire.[23] Here the difference between solvent and solute activation energies of diffusion is written as

$$Q = Q_2 - Q_1 = (H_2 - H_1) + (E_{v2} - E_{v1}) + C, \tag{5}$$

where, as throughout this paper, we follow the standard practice that subscript 2 refers to the solute, subscript 1 to the solvent. The H's are enthalpies of motion and the E_v's are enthalpies of vacancy formation and $C = -R\,[\partial \ln f_2/\partial(1/T)]$ and should not be too temperature sensitive except in extreme circumstances. Now E_{v2} is simply the energy of forming a vacancy next to an impurity and is given by

$$E_{v2} = E_{v1} + E_b, \tag{6}$$

where E_b is the same as in Eq. (4) and is given by LeClaire as

$$E_b = -(Z_i Z_v e^2 \alpha/a)\, e^{-qa}, \tag{7}$$

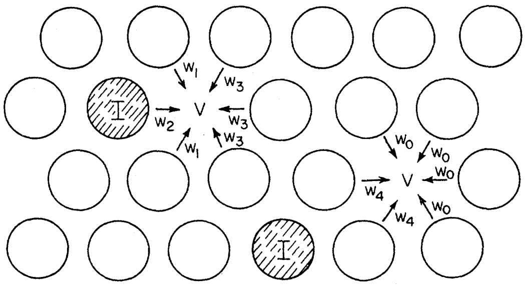

FIG. 4. Model of vacancy mechanism. Shown is a (111) plane of a fcc lattice indicating the jump frequencies of atoms into both associated and dissociated vacancies. Key: open circle, solvent atom; filled circle, impurity atom; missing circle, vacancy.

where Z_i, the effective charge for an impurity on a lattice site, equals the host valence minus the impurity valence; Z_v, the vacancy's effective charge, equals the host valence; e is the charge of one electron, a the separation, q the screening constant, and α a constant which depends on the Z's. This is simply to represent the vacancy and impurity as point charges interacting via a screened electric field. This means that if a substitutional impurity has valence less than its host's, then it repels vacancies. Such would be the case for mercury in lead. By consideration of the saddle-point configurations' electrostatic energies, LeClaire has also shown that the difference of the energies of motion has a similar form and so, neglecting C, we get

$$\begin{aligned} Q &= (H_2 - H_0) + E_b \\ &= Z_v Z_i e^2 \alpha\,(16/11a)\, e^{-11qa/16}. \end{aligned} \tag{8}$$

While this treatment has had its greatest success describing electropositive impurities in the noble metals, and in fact gives rather poor quantitative agreement for electronegative impurities, for reasons which are not well understood[24] the signs of the energy differences predicted for other cases are always correct. We therefore expect mercury to diffuse more slowly than the lead itself.

The computations of March and Murray[25] of the electrostatic potential surrounding a point charge in an electron gas further indicate that in polyvalent metals the electron density is so high that charges are screened in distances less than an atomic radius. As a result E_b should be nearly zero and $H_2 - H_1$ should be very small, and by this argument all impurities in these hosts should diffuse at essentially the same rate as the host itself.[6,26] The behaviors of indium and mercury in tin,[16] and of tin[14] and thallium[12] in lead, are in agreement with these ideas. The diffusion of various impurities in aluminum has also been cited in this connection,[6,26] but recent NMR work by Rowland and Fradin,[27] which seems to indicate the presence of very high jump rates in these systems, suggests that they may be more complex than indicated by this simple treatment and deserve further study. The essential theoretical prediction for the diffusion of mercury in lead remains, however, that it should be less than or approximately equal to the self-diffusion rate of the lead itself.

Our next concern is with the relation between the three independent frequency ratios in the vacancy model and such observable properties as the diffusivities of host and impurity, their correlation coefficients, and linear enhancement coefficients. The first such relation, between the diffusivities of solute (D_{20}) and solvent (D_{10}) in the pure solvent, was shown by Peterson[24] to be

$$\frac{D_{20}}{D_{10}} = \frac{f_2}{f_0}\,\frac{w_2}{w_1}\,\frac{w_4}{w_0}\,\frac{w_1}{w_3}\,. \tag{9}$$

This result follows from Lidiard's relations[17] for D_{20} and D_{10}:

$$D_{20} = \tfrac{1}{6} z a^2 f_2 w_2\, e^{-E_{v2}/RT}, \tag{10a}$$

$$D_{10} = \tfrac{1}{6} z a^2 f_0 w_0\, e^{-E_{v1}/RT}, \tag{10b}$$

so that

$$\frac{D_{20}}{D_{10}} = \frac{f_2}{f_0}\,\frac{w_2}{w_0}\, e^{-(E_{v2}-E_{v1})}. \tag{11}$$

The desired relation follows by noting $E_{v2} - E_{v1} = E_b$ and applying Eq. (4). Here f_2 and f_0 are the respective correlation coefficients of diffusion. Manning[20] has carefully evaluated f_2 as a function of the three jump-frequency ratios and finds that

$$f_2 = \frac{1 + 3.5F(w_4/w_0)\,(w_3/w_1)}{1 + w_2/w_1 + 3.5F(w_4/w_0)\,(w_3/w_1)}\,, \tag{12}$$

where

$$F(X) = 1 - \frac{1}{7}\left(\frac{10X^4 + 180.5X^3 + 927X^2 + 1341X}{2X^4 + 40.2X^3 + 254X^2 + 597X^2 + 435}\right). \tag{13}$$

In conjunction with the present work we compared this result with an analysis of the type done by Howard[18] where the vacancy was allowed to range up to three atom steps from the impurity. Those which exceeded this limit were assumed to return at random. All three jump frequencies were varied from 10^{-6} to 10^{+6} and over this range the results were always within 1% of the values predicted by Eqs. (12) and (13). When all three ratios are set to unity, corresponding to self-diffusion, Eq. (11) gives f_2 equal to 0.78143, in excellent agreement with the value $f_0 = 0.78146$ calculated by Compaan and Haven.[28] Correlation coefficients are measured experimentally using the isotope effect, as has been thoroughly discussed by Peterson.[24]

The remaining experimental parameters which depend on the three jump ratios are the linear enhancement coefficients b_{11} and b_{21}. Hoffman, Turnbull, and Hart[29] first showed that an enhancement of the self-diffusion would result from impurity diffusion by a vacancy mechanism, but it remained for Howard and Manning[21] to extend Lidiard's theory of this effect[17] to include solvent atom correlations and obtain

$$b_{11} = -18 + \frac{4}{f_0}\left(\frac{w_4}{w_0}\right)\left(\chi_1 \frac{w_1}{w_3} + \frac{7}{2}\chi_2\right), \tag{14}$$

where χ_1 is the correlation coefficient for w_1 jumps and χ_2 is the correlation coefficient for w_3 jumps. Howard and Manning tabulate values of χ_1 and χ_2 for a variety of values of the ratios w_2/w_1, w_4/w_0, and w_3/w_1. Miller[8,30] has extended Lidiard's analysis to the problem of impurity enhancement and obtains

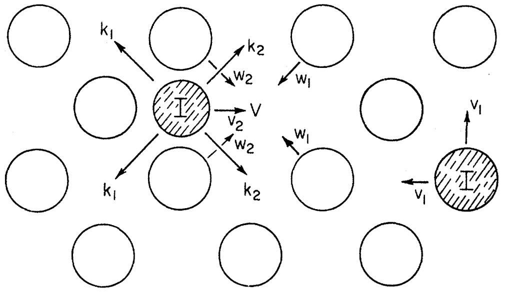

FIG. 5. Model of interstitial-vacancy (I-V) mechanism. Shown is (100) plane of fcc structure indicating the jump frequencies about both the I-V pair defect and about a substitutional impurity atom. Same key as in Fig. 4.

$$b_{21}=11\,(e^{-E_{b2}/RT}-1) \tag{15}$$

subject to the assumptions that E_{b2} is the binding energy of a second impurity to the impurity-vacancy pair, that both these impurities exchange with the vacancy with the same frequency w_2, as does a single impurity, and that the correlation coefficients for both these jump types are the same. In this admittedly coarse approximation, b_{21} is independent of the jump-frequency ratios and depends only on the binding energy E_{b2}.

There are, then, three independent jump-frequency ratios and three formulas, Eqs. (9), (12), and (14), relating them to three experimental parameters. It is therefore possible to determine the ratios by measuring the parameters or, barring this, to determine a range of acceptable values for one parameter consistent with the theory if the other two have been measured. This has been discussed by Peterson[24] and Howard and Manning[21] and provides a means of testing the applicability of the vacancy model to a given diffusion system. Such an analysis led Miller[6] to conclude that cadmium did not diffuse in lead by a vacancy mechanism. The case of particular interest to the present work is the one in which D_{20}/D_{10} and b_{11} have been measured but f_2 has not. In this case it is possible to calculate what values f_2 might assume and still be consistent with the theory. This is done by assuming a value for w_4/w_0 and calculating, by successive approximations, the values of w_3/w_1 and w_2/w_1 and so f_2 required to produce the measured values of b_{11} and D_{20}/D_{10}. This is done for all values of the ratio w_4/w_0 for which solutions exist, which generates an allowed range of values for f_2 to which later experimental results may be compared. Howard and Manning[21] did this for several impurities in silver, and in Sec. IV C we shall present the results of such an analysis using the values of b_{11} and D_{20}/D_{10} from the present work.

A second test of the diffusion mechanism can also be made for any particular system. This results from an observation by Miller[6] that for a given ratio of D_{20}/D_{10} there exists a minimum value of b_{11} consistent with the vacancy mechanism. This is given by

$$b_{\min}=-18+1.9448\,(D_{20}/D_{10}) \tag{16}$$

under the conditions that $w_4/w_0\rightarrow 0$ and $w_2/w_1\rightarrow\infty$; w_3/w_1 is simultaneously forced to zero by Eq. (4). Physically these conditions may seem unlikely to occur simultaneously, but currently there are no theoretical grounds for their modification. It was primarily the result that the measured b_{11}'s for the diffusion of cadmium in lead were less than $b_{\min}$ which forced Miller to develop the theory of diffusion by interstitial-vacancy pairs. The predictions of this model will be summarized in Sec. IV B.

B. Interstitial-Vacancy Pair Mechanism

This mechanism was developed by Miller primarily to explain the diffusion of cadmium in lead, and is discussed in detail in Refs. 7, 8, and 30. In the following few paragraphs we shall give a brief description of the theory and its major predictions.

Figure 5 shows a piece of fcc lattice containing an interstitial-vacancy pair, hereafter an I-V pair, and a substitutional impurity. Pairs are created with frequency v_1 and annihilated with frequency v_2. They are dissociated by either interstitial jumps k_1 or solvent jumps w_1 and associated by solvent jumps w_3. Jumps which preserve the association are solvent jumps w_2 and interstitial jumps k_2. Since in equilibrium there will be relations like Eq. (4) between v_2 and v_1 and also between k_1, w_1 and w_3, we see that there are therefore five independent frequencies in the model. Miller's interest centered on the cases where the pairs are tightly bound and hence

$$k_2,\ w_2\gg k_1,\ w_1, \tag{17}$$

which is to say, the case where the pairs dissociate only infrequently. In this limit the model behaves as follows: A pair is formed by a v_1-type jump and then the position of the interstitial is randomized by k_2-type jumps. At some point the vacancy moves by a w_2-type jump and the interstitial again randomizes by k_2-type jumps before it decays back into a substitutional by a v_2-type jump. This short description clearly shows the source of the model's two major results. First, when $k_2\gg w_2$, the net effect of all the shuffling is that every time an impurity makes an effective jump a solvent atom has moved in the opposite direction and thus

$$b_{11}\approx D_{20}/D_{10}. \tag{18}$$

Second, since the majority of impurity jumps are of type k_2, which center about the vacancy position, they will be highly correlated and f_2 will be

TABLE VIII. Summary of the predictions of the vacancy model and the I-V pair model.

Quantity	Vacancy-model prediction	I-V-pair model prediction
D_{20}/D_{10}	$D_{20} \approx D_{10}$	Ratio may be large
b_{11}	$b_{11} \geq b_{\text{min}} = -18 + 1.9448\,(D_{20}/D_{10})$	$b_{11} \lesssim f_0(D_{20}/D_{10})$
b_{21}	$b_{21} = 11\ (e^{-E_{v2}/RT} - 1)$	$b_{21} = 4(e^{-C/RT} - 1)$
f_2	$0 \leq f_2 \leq f_{\text{max}} \approx 0.4$	f_2 is very small

very small, approaching

$$f_2 \approx 0, \tag{19}$$

and the diffusion of the impurity will be controlled by w_2-type jumps.

Miller then proceeds to apply an analysis of the type of Lidiard[17] to this system, calculating D_{20}, b_{11}, and f_2 in terms of the indicated jump frequencies and the energies of the defects. His first result is

$$D_{20} = s^2 \exp\left(\frac{-(E_{v1} + I + B)}{RT}\right) \times \left(\frac{(4k_2 + v_2)(4w_2 + 8w_1 + 12k_1)}{4w_2 + 8w_1 + 4k_2 + 8k_1 + v_2} + 8k_1\right), \tag{20}$$

where I is the formation energy of a free interstitial, B its binding energy to a vacancy, and s the jump distance. In the regime where the interstitial jump frequencies are large, we have k_2, $v_2 \gg w_2$, w_1, k_1, and the latter slow jump frequencies become rate controlling. In this limit, Eq. (20) becomes

$$\frac{D_{20}}{D_{10}} = \frac{2(w_2 + 2w_1 + 5k_1)}{w_0 f_0}\, e^{-(I+B)/RT}, \tag{21}$$

and so long as the inequalities hold, D_{20}/D_{10} may be made arbitrarily large by increasing w_2/w_0, etc. An expression for b_{11} is obtained in a similar manner by considering the jumps of the solvent atoms affected by the defect, assuming that all their correlation coefficients are the same, i.e., that

$$f(w_2) = f(w_1) = f(w_3) = f_0\,. \tag{22}$$

With this approximation

$$b_{11} = \frac{f_0 D_{20}}{D_{10}}\left(1 + \frac{5k_1}{w_2 + 2w_1}\right)^{-1} \leq \frac{f_0 D_{20}}{D_{10}}\,, \tag{23}$$

and, for tightly bound pairs, where k_1 is very small, Eq. (23) approaches Eq. (18), which describes the experimental results for cadmium in lead within the accuracy of the experiments. Indeed, because of the errors in his b_{11}'s, Miller is not able to distinguish between the possible relationships $b_{11} = D_{20}/D_{10}$ and $b_{11} = f_0 D_{20}/D_{10}$. He is, however, able to conclude that if the cadmium is diffusing as I-V pairs then they must be tightly bound, since $b_{11} \gtrsim f_0 D_{20}/D_{10}$ implies that $k_1 \approx 0$.

The development of an expression for b_{21} in this model proceeds exactly as in the case of the vacancy except that the counting of configurations is different, and an essentially identical result is obtained. This is

$$b_{21} = 4(e^{-C/RT} - 1), \tag{24}$$

where C is the binding energy of a second substitutional impurity atom to the diffusing I-V pair.

We conclude our presentation of Miller's I-V pair model with the observation that, since there are so many jump frequencies, it is no longer possible to calculate an allowable range of values for f_2, if measurements of b_{11} and D_{20}/D_{10} have been made. Even neglecting all dissociative processes and assuming that $k_1 = w_1 = 0$ does not help, for this is just the case for which $b_{11} = f_0 D_{20}/D_{10}$ and we are left with two equations for three unknowns. All in fact that can be said is that if, indeed, k_2 is very large, then f_2, which is essentially the term multiplying $4k_2 + v_2$ in Eq. (20), will be very small[7] and this is just what is noted from the isotope experiment for cadmium in lead.[31]

C. Comparison with Present Data

Now that we have examined the vacancy and I-V pair models, we can compare their predictions with our measurements on diffusion in the Pb:Hg alloy system. For the purpose of easy reference, these predictions are summarized in Table VIII. The value of f_{max} listed for the vacancy model results from a calculation of the range of values of f_2 which are consistent with the measured values of b_{11} and D_{20}/D_{10} in the manner described earlier. This will be fully discussed later.

D_{20}/D_{10}. The limits predicted for D_{20}/D_{10} by both models are listed in the first row of Table VIII. In the vacancy model, because of screening and repulsion of vacancies by the mercury impurity, this ratio should be ≤ 1.0. For the I-V pair model, on the other hand, Eq. (21) shows that the ratio may become arbitrarily large for appropriate values of k_2 and w_2. Table IX contains a summary of our experimental results in forms convenient to the present comparisons and shows that in all cases

TABLE IX. Tabulated values of D_{20}/D_{10}, b_{min}, b_{11}, and $b_{11}(D_{20}/D_{10})^{-1}$ from this work for comparison to predictions of vacancy and I-V pair models.

T (°C)	D_{20}/D_{10}	b_{min}	b_{11}	$b_{11}(D_{20}/D_{10})^{-1}$
294.6	14.3	9.8	22.1 ± 3.0	1.5 ± 0.20
274.1	15.7	12.5	23.2 ± 1.6	1.48 ± 0.10
251.8	17.6	16.1	27.2 ± 2.3	1.54 ± 0.13
225.2	20.2	21.2	28.2 ± 3.2	1.40 ± 0.15

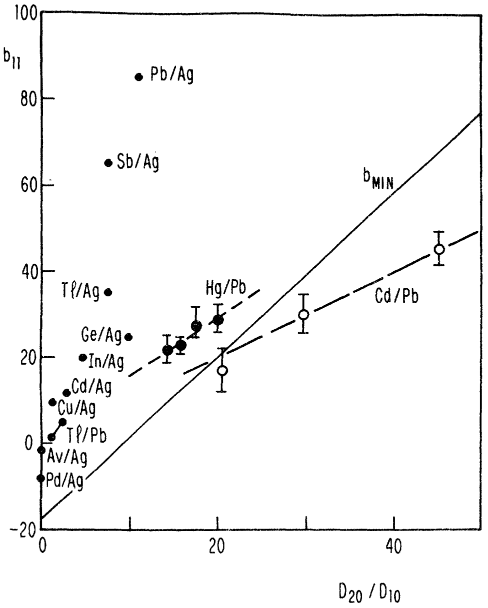

FIG. 6. Enhancement of self-diffusion in Pb : Hg alloys shown in comparison with $b_{\min}$ and values for other systems.

D_{20}/D_{10} is greater than 14. This is acceptable in the I-V pair model but not in the vacancy model as it is presently understood.

b_{11}. The second row of Table VIII gives Eqs.(16) and (23) which may be compared to the values given in Table IX. This shows that, in contrast to the case of cadmium in lead, all the values of b_{11} are greater than their associated values of $b_{\min}$. This is still a very unusual system, however, as is made clear by Fig. 6, where the b_{11}'s for both mercury and cadmium in lead are plotted versus D_{20}/D_{10}. Also included in the figure are the function $b_{\min}$ and values for a variety of other systems which are thought to diffuse by a vacancy mechanism.[6] These latter fall exclusively in the upper-left-hand corner of the figure which, referring to Eqs. (9)–(12), physically means that when the impurity can jump easily and w_2 is large, the nearest neighbors can also jump easily and w_1 also gets large. This allows f_2 to stay near unity and allows D_{20}/D_{10} to become large. It should be emphasized that, while it may be *possible* be keep b_{11} small while letting D_{20}/D_{10} get large, in the manner of obtaining $b_{\min}$, this would be *unusual* in terms of our experience with systems where we are more certain that diffusion proceeds by a vacancy mechanism. The primary effect of Fig. 6 then, is to emphasize that the diffusion of mercury in lead seems more similar to the case of cadmium in lead than to any of the other systems.

The measured values of b_{11} do not agree very well with the I-V pair model either. Table IX shows that typically $b_{11}(D_{20}/D_{10})^{-1} \approx 1.5$ instead of being $\lesssim 0.78$ as required by Eq. (23). The experimental accuracy of these values is such that the diagreeement is significant. Further, Eq. (23) also shows that no assumptions about whether or not the pairs are tightly bound can influence this result. The only assumptions made in the derivation of this relation were that the interstitial jump frequencies k_2 and v_2 were much higher than any other frequencies in the model and that as a result all the solvent atom jumps had the same partial correlation coefficients, as shown in Eq. (22). If we relax the assumption that k_2, $v_2 \gg w_2$, w_1, k_1, the Eq. (22) is no longer valid and the derivation of Eq. (23) breaks down, and the problem requires complete reanalysis. For the present we can simply conclude that, in their present forms, neither model gives a fully satisfactory description of the enhancement of the self-diffusion of lead by additions of mercury.

b_{21}. Row three, Table VIII, recalls the prediction o both models about b_{21}, the enhancement of the mercury diffusion in Pb: Hg alloys by additions of mercury. These relations, Eqs. (15) and (24), are nearly identical in form and are easily compared to the data by plotting $\ln(\frac{1}{11}b_{21}+1)$ and $\ln(\frac{1}{4}b_{21}+1)$, respectively, versus $1/T$. This is done in Fig. 7, which shows that the data agree with either expression within experimental error. The values of the energy terms in the exponentials, as determined from these plots, are $E_{b2} \approx 2$ kcal/mole for the vacancy mechanism, or $C \approx 3$ kcal/mole for the I-V pair mechanism. The values of b_{21}, then, are readily explained by either model. Comparison

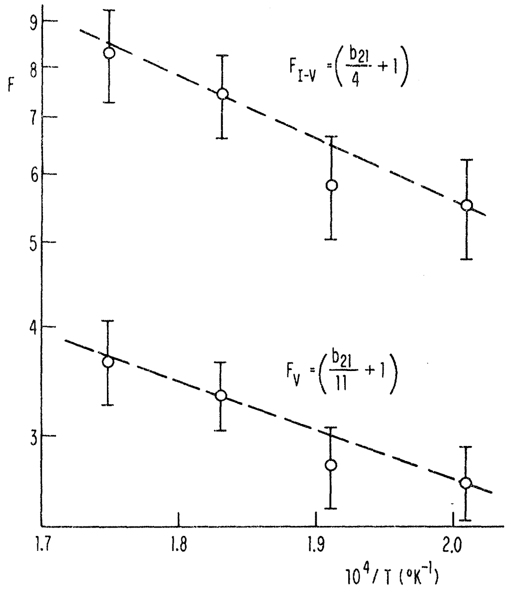

FIG. 7. Comparison of experimental data on b_{21} values with predictions of vacancy model and I-V pair model.

TABLE X. Values of f_2 consistent with b_{11} and D_{20}/D_{10} as calculated from vacancy model. D_{20}/D_{10} and b_{11} are measured, w_4/w_0 is assumed, and w_3/w_1, w_2/w_1, and f_2 are calculated.

T (°C)	b_{11}	w_4/w_0	w_3/w_1	w_2/w_1	f_2
294.6	22.1	10^2	No solution		
		2	No solution		
		1	0.114	67	0.019
		$\frac{1}{2}$	0.040	4.7	0.194
		$\frac{1}{10}$	0.0058	1.81	0.361
		$\frac{1}{100}$	0.00058	1.90	0.346
	25.4	$\frac{1}{100}$	0.00054	1.51	0.398
	18.8	$\frac{1}{100}$	0.00064	2.54	0.282
294.6	22.1 ± 3.0	$\frac{1}{100}$	0.00058	1.90	$0.346^{+0.052}_{-0.064}$
274.1	23.2 ± 1.6	$\frac{1}{100}$	0.00054	2.01	$0.333^{+0.027}_{-0.031}$
251.8	27.3 ± 2.3	$\frac{1}{100}$	0.00050	2.12	$0.320^{+0.035}_{-0.040}$
225.5	28.2 ± 3.2	$\frac{1}{100}$	0.00047	2.92	$0.265^{+0.050}_{-0.053}$

of E_{b2} to values computed by Miller for various impurities in silver and C to his value for cadmium in lead[8,30] shows that neither of our values is unreasonable.

f_2. It is possible, as was shown in Sec. IV B, to use relations (9) and (12)–(14), in conjunction with Howard and Manning's values for χ_1 and χ_2, to calculate the range of values of f_2 consistent with the measured values of b_{11} and D_{20}/D_{10} assuming the diffusion occurs by a vacancy mechanism. The results of such calculations are presented in Table X. The calculations at 294 °C are shown in detail, giving the consistent values of w_2/w_1, w_3/w_1, and f_2 for decreasing values of w_4/w_0. It is clear that there are values of w_4/w_0 for which solutions do not exist and also that as w_4/w_0 gets very small, w_2/w_1 and f_2 reach a maximum. This value is denoted $f_{\max}$ and its values at all four temperatures are listed, along with the standard errors which result from the standard errors in the values of the various b_{11}'s. Since ΔK is less than unity, $f_{\max}$ is an upper bound for $f\Delta K$ in the isotope experiment and therefore provides a definitive test of the applicability of the vacancy model this system. Unfortunately, as noted earlier, no similar test exists for the I-V pair model as Miller developed it. All that can be said is that it should be very small. If such a result were measured, then, it would not help us to distinguish between the models since there is also a range of values of w_4/w_0 for which f_2 is likewise very small.

V. CONCLUSIONS

In general aspect the diffusion of mercury in lead appears to be very similar to that of cadmium in lead. The bulk diffusivities and activation energies of diffusion are very nearly the same. Further, when b_{11} is plotted versus D_{20}/D_{10}, the enhancement effects also appear more similar to the cadmium-in-lead case than to any system where diffusion takes place by a vacancy mechanism. The vacancy mechanism is also unable to explain how mercury might diffuse so rapidly in a system with so high an electron concentration. Since the I-V pair model seems to give a good interpretation of the behavior of cadmium in lead, we have attempted to apply it to the present case as well. This gives, in fact, an adequate explanation of certain phenomena, particularly the fast-diffusion behavior and the temperature dependence of b_{21}. The I-V pair model is, however, completely incapable in its present form of producing a value of $b_{11}(D_{20}/D_{10})^{-1}$ greater than unity, the experimental result.

What this all suggests is that diffusion in both systems may indeed occur by the same, or at least similar, mechanisms, but that perhaps the assumptions used in the development of the model are too extreme to allow a proper description of the mercury diffusion. This further suggests that the I-V pair model should be reexamined without assuming k_2, $v_2 \gg w_2$, w_1, k_1 or possibly with a different set of simplifying assumptions. In this way we might preserve the good features of the present I-V pair model, since we should still be able to get fast impurity diffusion and since the derivation of the expression for b_{21} does not explicitly depend upon these assumptions, yet possibly be able to relax Eq. (23) to allow values of $b_{11}(D_{20}/D_{10})^{-1}$ greater than unity. Such a model is developed in the following paper.[32]

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Modified Model of Diffusion by Interstitial-Vacancy Pairs

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In order to adequately describe the diffusion of mercury in lead, the interstitial-vacancy pair model is redeveloped in a form which only allows impurity jumps which create or annihilate the pair and nearest-neighbor exchanges with the vacancy by solvent atoms, but in which the correlation coefficients for these three jump types are calculated explicitly. These calculations are done numerically for a range of jump frequencies using the formalism of Howard. In this new model, expressions are developed for the diffusivity, correlation coefficient, and enhancement of the solvent diffusivity which show behavior similar to the older models except that now $f_0 < b_{11}/[D_2(0)/D_1(0)] \leq 3.80$, a feature true of the diffusion of both mercury and cadmium in lead which is not explicable in terms of the older model. This model is also in adequate agreement with the other features of diffusion in these two systems. It is demonstrated, however, that a complete description of the defects' natures requires measurements of a nondiffusive sort, and some suggestions are made.

I. INTRODUCTION

The diffusion of mercury in lead was reported in the preceding paper[1] and shown not to be well described by any of the currently available models of diffusion, including the vacancy and interstitial-vacancy pair (I-V pair) models. It seemed possible, however, that, if the I-V pair model could be extended by removing or modifying certain of the assumptions made in the development of Miller,[2] it might be capable of describing the experimental results. The main object of the present paper, then, is to redevelop the I-V pair model, but with a different set of assumptions about the various jump frequencies and, most importantly, without assuming that the correlation coefficients of the impurity jumps and of the nearest-neighbor jumps are equal to the correlation coefficient for the solvent jumps in the pure metal. They will instead be calculated in terms of the model's jump frequencies in the manner of Mullen[3] and Howard.[4]

The formalism developed by Howard,[4] Howard and Manning,[5] and Manning[6] for calculating correlation coefficients is particularly powerful and