Interstitial substitutional model for the anomalous diffusion in Pb and Pb alloys

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(Received 6 August 1979; revised manuscript received 17 December 1979)

A model is proposed which involves interstitial, substitutional, and disubstitutional defects along with the equilibrium fraction of each defect type. The lead diffusivity data from a variety of experimental measurements are reinterpreted in terms of this model. Both enhancement and de-enhancement diffusivity results as a function of impurity content are discussed for both impurity and self-diffusion. Impurity diffusion in the limit of small impurity concentration is analyzed. The resulting system reduces to a two-defect interstitial-substitutional model. Questions pertaining to the large variation in the measured activation energies and volumes are discussed. The model explains why impurity-lead diffusion couples that appear to be predominantly interstitial or substitutional in nature give activation volume results which are not characteristic of either an interstitial or substitutional mechanism. The isotope effect has been reanalyzed in terms of the proposed model and the small values of $f\Delta K$ of 0.12, 0.25, and 0.23 for Cd, Ag, and Cu, respectively, in Pb are interpreted in terms of small changes in the interstitial and substitutional energy states, amounting to about 2×10^{-4} eV/atomic mass unit. The equilibrium fraction of interstitial defects as a function of temperature and pressure was calculated for each of the diffusion couples, Cu, Ag, Au, Ni, Pd, Pt, Zn, Cd, Hg, and Sn in Pb, as was the pressure and temperature dependence of pure interstitial substitutional diffusivity.

INTRODUCTION

Experiments as early as 1896 on the diffusion of Ag and Au in Pb reported results which were 10^3–10^4 times larger than for Pb self-diffusion. Subsequent measurements were made which verified that these results were characteristic of bulk diffusion and not the result of dislocations, grain boundaries, or dissolved impurity atoms. It was concluded that the diffusivity was proceeding by some type of interstitial mechanism. Over the intervening years there has been a great deal of interest and a wide variety of experimental results reported concerning the anomalous diffusion in lead and other high-Z polyvalent solvents. The lead system which is typical of this class has probably received the greatest amount of attention. Numerous measurements involving the noble and near-noble metal impurity diffusion in Pb and Pb alloys have been made. These include diffusion in Pb of Cu, Ag, Au, Ni, Pd, Pt, Zn, Cd, and Hg, along with Pb self-diffusion.[1-22] The diffusion of Sn, Tl, Bi, and Na in Pb have also been measured.[23-25] A model will be presented, which, it is hoped will tie together all of the experiments from the many investigators.

A model which is consistent with all of the measurements has been rather slow in developing. Very early, Seith and Keil,[26] upon finding no enhancement for Au diffusion in Pb(Au) alloy, suggested the interstitial impurity defect to explain the anomalous diffusivities of Ag and Au in Pb. Frank and Turnbull,[27] trying to explain the anomalous diffusion of Cu in Ge, introduced the so-called

dissociative mechanism in which the impurity is dissolved in both interstitial and substitutional sites. This mechanism has been quite successful in explaining many aspects of the anomalous diffusion in the high-Z polyvalent hosts. Miller[28] in late 1969 introduced the interstitial-vacancy bound pair (iv pair) in order to explain the enhancement of Pb self-diffusion in Pb(Cd) alloys and the isotope effect[29] for Cd in Pb. Decker, Candland, and Vanfleet applied an equilibrium model[12] involving substitutional, interstitial, and interstitial-vacancy pairs to explain the widely varying diffusivities, activation energies, and activation volumes in the ambient and high-pressure data for the diffusion of Ag, Au, Cu, Pd, Cd, Hg, Ni, and Zn impurities in Pb. Warburton's measurement on the diffusion of Hg and Pb in dilute Pb(Hg) alloys[18] indicated a problem with the substitutional, interstitial, and iv-pair model. This model then completely broke down when Warburton found a strong de-enhancement for Au impurity diffusing in Pb(Au) alloys.[30] In order to explain the de-enhancement effects, Warburton suggested PbAu and Au₂ dimers along with possible higher-order impurity clusters. The resistivity measurements of Cohen, Turnbull, and Warburton for small additions of Au in Pb were interpreted to indicate higher-order defect clusters[31] of Au₃ and Au₄ at single substitutional sites in the Pb. The isotope measurements for Cd, Ag, and Cu in Pb have been very puzzling.[6,29,32] The $f\Delta K$ values are very small, suggesting a defect such as an iv pair which has a highly correlated motion.

In summary, past investigators have found the

enhancement of self-diffusion in dilute Pb(Au), Pb(Ag) (Ref. 22), Pb(Cd) (Ref. 15), and Pb(Hg) (Ref. 18) alloys too small to be consistent with dissolved substitutional impurity and too large to be consistent with interstitial impurity. Enhancement of impurity diffusion for Hg in Pb(Hg) (Ref. 18) was found to be large and positive; for Ag in Pb(Ag) (Ref. 33) it was very nearly zero; for Au in Pb(Au) (Ref. 30) it is large and negative; for Ni in Pb(Ni) and Cd in Pb(Cd) (Ref. 34), it starts out sharply negative, then goes positive at higher impurity concentrations. The impurity diffusivities for Cu, Ag, Au, Ni, Pd, Pt, Zn, Cd, Hg, and Sn range almost continuously over more than five orders of magnitude. The activation energies range from 8.2 for Cu to 25.7 kcal/mole for Pb self-diffusion. The activation volumes range from 0.04 for Pd to 0.75 atomic volumes for self-diffusion. The isotope effect for Cd, Ag, and Cu in Pb have $f \Delta K$'s of 0.12, 0.25, and 0.23 which seem unbelievably small for substitutional or interstitial related mechanisms. The impurity diffusivity of Au in dilute Pb(Pd) and Pb(Ag) alloys[9] is strongly de-enhanced.

It appears that with almost every new experiment there has been a need to introduce a new defect in order to explain the new result. It is the intention here to show that all of the experimental results can be explained in terms of interstitial, substitutional, and disubstitutional doublet defects.

DIFFUSION MODEL

A macroscopic model for enhancement–de-enhancement for both impurity atom and self-diffusion as a function of impurity concentration is proposed. The model is based on the premise that the impurity atoms exist as interstitial (i), substitutional (s), and doublet (d) defects. Because of the rather open lattice and the relatively strong screening effects in the Pb, the most probable doublet configuration has been assumed to be two impurity atoms symmetrically located and oriented in the [100] direction at a substitutional site. The addition of other types of singlets, such as iv pairs, or doublets interstitially located will not alter the form of the result.

The effective impurity diffusivity assuming a uniform impurity concentration x in the sample can be written

$$D(x) = \frac{c_i(x)}{x} D_i(x) + \frac{c_s(x)}{x} D_s(x) + \frac{2c_d(x)}{x} D_d(x),   (1)$$

where c_i, c_s, c_d and D_i, D_s, D_d are the concentrations and diffusivities of interstitial, substitutional, and doublets, respectively, and x is the total

impurity concentration. Conservation of impurities requires

$$x = c_i + c_s + 2c_d.   (2)$$

It should be noted that the concentration dependence of $D(x)$ involves changes in both the defect diffusivities $D_i(x)$, $D_s(x)$, and $D_d(x)$ and the defect fractions $c_i(x)/x$, $c_s(x)/x$, and $c_d(x)/x$.

It will be assumed that the singlets and doublets are in chemical equilibrium with rate constants k_1 and k_2. Thermodynamic equilibrium will be assumed between the two-particle doublet state and the two-particle interstitial-substitutional state. The two states have a binding energy B between them and the two-particle doublet has been taken to be the lower energy state.[9]

$$
\begin{array}{c}
i + s \overset{k_1}{\underset{}{\rightleftharpoons}} d \\
+ \\
v \\
\text{⇊} \, k_2 \\
s
\end{array}
\qquad (3)
$$

$$c_d = k_1 c_i c_s, \quad c_s = k_2 c_i c_v,   (4)$$

where c_v is vacancy concentration.

Defining the quantities $q(x) = c_i(x)/x$, $q_0 \equiv q(0) = 1/(1 + k_2 c_v)$, $h(x) = 2/[1 + (1 + 4d_{21} x)^{1/2}]$, and $d_{21} = 2q_0(1 - q_0)k_1 = 6q_0(1 - q_0)e^{+B/RT}$ one obtains on combining Eqs. (2) and (4)

$$c_i(x)/x = q_0 h(x), \quad c_s(x)/x = (1 - q_0)h(x),$$
$$2c_d(x)/x = 1 - h(x).   (5)$$

Let us now consider the concentration dependence of $D_i(x)$ for interstitial impurity diffusion. It will be assumed that the diffusivity of an interstitial is altered from its value D_{i0}, which it has in the defect-free lattice, to D_{ii}, D_{is}, or D_{id}, whenever it finds itself in the near vicinity of another interstitial, substitutional, or doublet defect, respectively. The total number of interstices N_0 can be written

$$N_0 = N_{reg} + Z_{ii} N_i + Z_{is} N_s + 2Z_{id} N_d,   (6)$$

where N_{reg} is the number of defect-free interstices in the lattice, Z_{ii}, Z_{is}, and Z_{id} are the number of interstices per impurity atom in the vicinity of the N_i, N_s, and N_d impurity defects, respectively, where the diffusivity is altered. Writing $D_i(x)$ as a weighted average of the interstitial diffusivity, one obtains

$$D_i(x) = \frac{N_{reg}}{N_0} D_{i0} + Z_{ii} \frac{N_i}{N_0} D_{ii}$$
$$+ Z_{is} \frac{N_s}{N_0} D_{is} + 2Z_{id} \frac{N_d}{N_0} D_{id}.   (7)$$

Using similar definitions for the concentration dependence for substitutional and doublet diffusion, and assuming that the number of lattice sites, the number of host atoms, and the number of interstices (fcc lattice) are about equal, one obtains

$$D_k(x) = D_{k0} + c_i Z_{ki}(D_{ki} - D_{k0})$$

$$+ c_s Z_{ks}(D_{ks} - D_{k0}) + 2c_d Z_{kd}(D_{kd} - D_{k0}) , \qquad (8)$$

where k takes the values i, s, and d corresponding to interstitial, substitutional, and doublet diffusion. Combining Eqs. (1), (4), (5), and (8) gives the total concentration dependence of the impurity diffusivity:

$$D(x) = q_0 h D_{i0} + (1 - q_0) h D_{s0}$$

$$+ xh^2[q_0^2 \mathfrak{D}_{ii} + (1 - q_0)^2 \mathfrak{D}_{ss}$$

$$+ q_0(1 - q_0)\mathfrak{D}_{is} + d_{21}D_{d0}]$$

$$+ x^2 h^3 d_{21}[q_0 \mathfrak{D}_{id} + (1 - q_0)\mathfrak{D}_{sd}] + x^3 h^4 d_{21}^2 \mathfrak{D}_{dd} , \qquad (9)$$

where $\mathfrak{D}_{jk} = Z_{jk}(D_{jk} - D_{j0}) + Z_{kj}(D_{kj} - D_{k0})$ for $j \neq k$, and $\mathfrak{D}_{kk} = Z_{kk}(D_{kk} - D_{k0})$.

Assuming that the self-diffusivity is altered from D_0^s, the value in the defect-free lattice, to D_i^s, D_s^s, D_d^s when the diffusing substitutional host atom is in the near vicinity Z_i^s, Z_s^s, Z_d^s of the N_i, N_s, and N_d defects, one obtains an expression similar to Eq. (9) for the impurity concentration dependence for self-diffusion.

$$D^s(x) = D_0^s + xh[q_0 Z_i^s(D_i^s - D_0^s) + (1 - q_0)Z_s^s(D_s^s - D_0^s)]$$

$$+ x^2 h^2 d_{21} Z_d^s(D_d^s - D_0^s) . \qquad (10)$$

Equations (9) and (10) can be cast into the following simplified form to more clearly show the concentration dependence for impurity diffusion (9') and for self-diffusion (10'):

$$D(x) = h(x)D(0)[1 + a_1 xh(x) + a_2 d_{21} x^2 h(x)^2$$

$$+ a_3 d_{21}^2 x^3 h(x)^3] , \qquad (9')$$

$$D^s(x) = D_0^s[1 + b_1 xh(x) + b_2 d_{21} x^2 h(x)^2] , \qquad (10')$$

where $D(0)$ and D_0^s are the impurity diffusivity and self-diffusivity in the limit as the impurity concentration x goes to zero and the a_i's and b_i's are concentration independent terms. It should be observed that Eq. (9') for the concentration dependence of impurity diffusivity is cubic in the concentration and Eq. (10') for the concentration dependence of self-diffusion is quadratic in the concentration. It is further noted, if it is not self-evident, that the enhancement model which is presented here for both impurity diffusion and self-diffusion breaks down for impurity concentrations greater than a few percent. When the cloud of Pb atoms which are nearest neighbors to the impurity atoms severely overlap with other Pb atom clouds, the assumptions are no longer valid.

ENHANCEMENT

The concentration dependence for impurity diffusion in Pb alloys is interesting in that it may either increase (enhance) or decrease (de-enhance) the diffusivity with increasing impurity concentration. One notes that $h(x)$ is a pure de-enhancement term and as a multiplicative factor in Eq. (9') may dominate the enhancement–de-enhancement of impurity diffusion. The cubic or quadratic polynomial in the parameter $xh(x)$ in Eq. (9') or (10') will have enhancement or de-enhancement contributions depending on whether the diffusivity near a defect is less than or greater than the diffusivity in the defect-free lattice.

It is further noted that if $d_{21}c_0$ the de-enhancement coefficient times the saturation solubility c_0 is large, then $h(x)$ decreases rapidly from unity as x approaches c_0. Conversely, if $d_{21}c_0$ is small then $h(x)$ is approximately 1 over the entire solubility range. Consider for example, the enhancement of the diffusivity of Au in Pb(Au) alloys.[30] It is found that $d_{21}c_0$ is in the range of 0.2–1.5, but x which is always less than the eutectic solubility of 2.7×10^{-3} is so small that the terms involving a_1, a_2, and a_3 in Eq. (9') are insignificant and the result is that $D(x)/D(0) \simeq h(x)$ which results in pure de-enhancement. A similar argument holds for Ag in Pb(Ag) (Ref. 33), except in this case $d_{21}c_0$ is much smaller than for Au and the result is that $D(x)/D(0) \simeq 1$. In the case of Hg in Pb(Hg) (Ref. 18) the saturation solubility is large at about 14% at 224 °C and $d_{21}c_0$ is found to be small at 0.065. Over the range of concentrations used in the experiment $h(x)$ is very nearly unity and Eq. (9') for the enhancement is dominated by the cubic polynomial in the impurity concentration x. It is found to increase rapidly with increasing impurity concentration and to produce almost pure enhancement. The impurity enhancement for self-diffusion Eq. (10') differs from the enhancement for impurity diffusion Eq. (9') in that there is no multiplicative de-enhancement factor $h(x)$ and it is quadratic in the product $xh(x)$.

Fits to Eq. (9') for the diffusion of Hg in Pb(Hg) (Ref. 18), Ag in Pb(Ag) (Ref. 33), and for Au in Pb(Au) (Ref. 30) are shown in Fig. 1. Fits to Eq. (10') for Pb self-diffusion into Pb(Ag), Pb(Au) (Ref. 22), Pb(Cd) (Ref. 15), and Pb(Hg) (Ref. 18) are shown in Fig. 2. The data were fitted assuming that the diffusivity of substitutional and doublet impurities is small compared to interstitial dif-
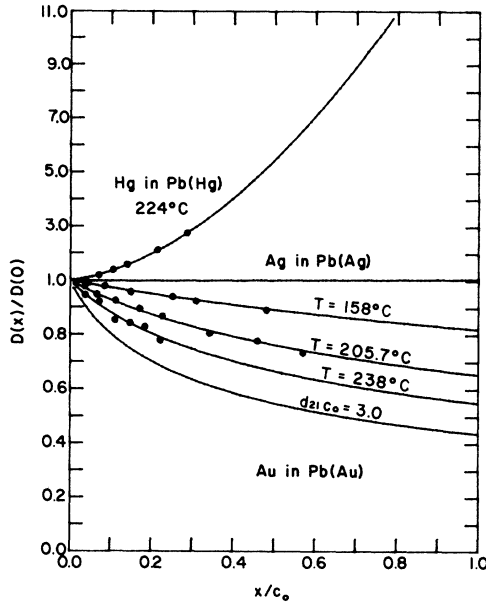
FIG. 1. Enhancement and de-enhancement of impurity diffusion in dilute Pb alloys versus the relative impurity concentration. c_0 is the saturation solubility at the indicated temperatures. The solid lines are curves fit to Eq. (9′) using the parameters from Table I. The curve marked $d_{21}c_0 = 3$ is a plot of the de-enhancement factor $h(x)$ for that value.

FIG. 2. Enhancement of Pb self-diffusion in dilute Pb alloys versus the relative impurity concentration. c_0 is the saturation solubility at the indicated temperature. The solid lines are curves fit to Eq. (10′) using the parameters from Table I.

fusion and terms in q_0^2 were neglected in Eq. (9). The parameters from a least-squares fit are shown in Table I. The fitting parameters for Pb self-diffusion in Pb(Ag), Pb(Au), Pb(Cd), and Pb(Hg) alloys indicate that the diffusion of Pb is
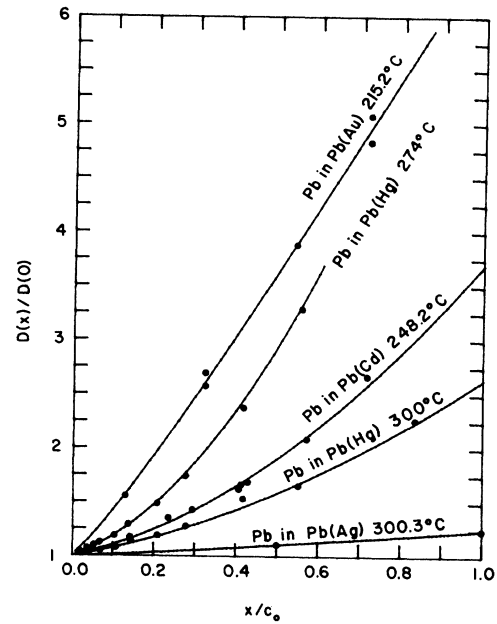
greatly enhanced when it is in the vicinity of a doublet defect. One notes that the values of $Z_d^s(D_d^s/D_0^s - 1)$ from Table I are found to range from 246 to 9340. Assuming that Z_d^s is of the order of 12, the number of nearest neighbors, then

TABLE I. Enhancement parameters for Eqs. (9) and (10).

Diffusion couple	T (°C)	$a_1 \sim Z_{is}(D_{is}/D_{io} - 1)$ or $b_{11} \sim Z_s^s(D_s^s/D_o^s - 1)$	$Z_{id}(D_{id}/D_{io} - 1)$ or $Z_d^s(D_d^s/D_o^s - 1)$	C_0 Solubility (atomic fraction)	d_{21}	
Pb in Pb(Ag) [a]	300	101 ± 10	246 ± 25	0.00177	7	± 7
Pb in Pb(Au) [a]	215	3300 ± 238	6931 ± 658	0.0012	784	
Pb in Pb(Cd) [b]	248	25 ± 4	9340 ± 5390	0.035	0.17 ±	0.09
Pb in Pb(Hg) [c]	274	20 ± 1	4632 ± 751	0.072	0.21 ±	0.04
Pb in Pb(Hg) [c]	300	19 ± 1	7216 ± 4300	0.036	0.11 ±	0.06
Hg in Pb(Hg) [c]	224	15 ± 1	1705 ± 601	0.139	0.46 ±	0.17
Au in Pb(Au) [d]	238	44 ± 5		0.0027	615	± 34
Au in Pb(Au) [d]	228	44 ± 5		0.0019	713	± 54
Au in Pb(Au) [d]	218	44 ± 5		0.0014	831	± 30
Au in Pb(Au) [d]	206	44 ± 5		0.00087	1008	± 32
Au in Pb(Au) [d]	178	44 ± 5		0.00029	1646	± 44
Au in Pb(Au) [d]	167	44 ± 5		0.00018	2030	± 82
Au in Pb(Au) [d]	158	44 ± 5		0.00012	2430	± 86
Au in Pb(Au) [d]	137	44 ± 5		0.00005	3808	±133

[a]Reference 22.
[b]Reference 15.
[c]Reference 18.
[d]Reference 30. Data for all temperatures fit simultaneously.

D_d^s/D_0^s ranges from about 20 to 750 which seems rather large to be accounted for by the frequency factor. It may be, however, that the strain field of the doublet has an attraction for vacancies and has a vacancy cloud surrounding it. This would strongly enhance the self-diffusivity in the vicinity of a doublet defect and factors of 10^3 or greater could easily be realized.

The linear enhancement–de-enhancement coefficient for impurity diffusion b_{21} is defined by $D(x)/D(0) = 1 + b_{21} x + \cdots$. Expanding $h(x)$ and other terms in Eq. (9') to first order in x yields $b_{21} = a_1 - d_{21}$ where a_1 is defined by Eqs. (9) and (9'). For small impurity concentrations one finds either enhancement or de-enhancement behavior depending on whether a_1 is larger or smaller then d_{21}. One notes from Table I that for Hg in Pb(Hg), b_{21} is positive and for Au in Pb(Au) it is very negative. The linear enhancement coefficient b_{11} for self-diffusion is defined in the usual way by $D^s(x)/D_0^s = 1 + b_{11} x + \cdots$. Expanding the terms in Eq. (10) to first order in x gives

$$b_{11} = b_1 = q_0 Z_i^s (D_i^s/D_0^s - 1)$$
$$+ (1 - q_0) Z_s^s (D_s^s/D_0^s - 1) .$$

From Table I it can seem that b_{11} ranges from about 20 for self-diffusion in Pb(Hg), to 101 for Pb(Ag), to 3300 for Pb(Au).

IMPURITY DIFFUSION

The analysis for impurity diffusion in pure Pb comes directly from Eq. (9) in the limit as the alloy concentration x approaches zero. In this case $h(0) = 1$ and it will be assumed that the concentration of impurity atoms is everywhere very small. This further implies the use of high-specific-activity radioactive sources and very thin boundary layers. Equation (9) reduces to a two-mechanism model involving interstitial and substitutional diffusion, and the equilibrium fraction q_0 of the im-

purities that are at interstitial sites:

$$D_0 = q_0 D_{i0} + (1 - q_0) D_{s0} . \tag{11}$$

The subscript 0 refers to the particular impurity species, $D_0 \equiv D(0)$, D_{i0} and D_{s0} refer to pure interstitial and substitutional diffusion of that species, and $q_0 = c_i(x)/x$ in the limit as x goes to zero. A representation for q_0 can be obtained if it is assumed that the substitutional and interstitial impurities form a two-energy state system with ΔG_q being the energy separation between states. Using Maxwell-Boltzmann statistics, taking the substitutional state as the ground state, and the interstitial as the excited state, one obtains

$$q_0 = 1/(e^{\Delta G_q/RT} + 1) . \tag{12}$$

The determination of the temperature and pressure dependence of q_0, D_{i0}, and D_{s0} from Eq. (11) requires an extremely wide range of temperatures and pressures to be measured for each diffusion couple. For the anomalous impurity diffusion in Pb there have been no measurements over a sufficiently wide range to allow determination of all three parameters. The diffusion of Au in Pb which has been measured over the widest range, 327–60 °C, shows no perceptible curvature. Decker et al.[9] have estimated that for Au in Pb one would have to go to temperatures as low as 50 K to see any significant curvature in Eq. (11). The data suggest that for the rapid diffusers in Pb, $q_0 D_{i0} \gg (1 - q_0) D_{s0}$, and hence from an Arrhenius plot of the diffusivity, one can only determine the product $q_0(T) D_{i0}(T) \simeq \exp(-\Delta G_q/RT) D_{i0}$. The ΔG_q term cannot be separated from the D_{i0} term.

The usual diffusion parameters which are published in the literature for small impurity concentrations are the activation energy and activation volume. These parameters are defined within small correction terms as $\Delta H = -[\partial \ln D_0/\partial(1/RT)]$ and $\Delta V = -RT(\partial \ln D_0/\partial P)$, and when applied to Eq. (11) yield

$$\Delta H = \frac{q_0 D_{i0} \Delta H_i + (1 - q_0) D_{s0} \Delta H_s + (D_{i0} - D_{s0}) q_0 (1 - q_0) \Delta H_q}{q_0 D_{i0} + (1 - q_0) D_{s0}} , \tag{13}$$

$$\Delta V = \frac{q_0 D_{i0} \Delta V_i + (1 - q_0) D_{s0} \Delta V_s + (D_{i0} - D_{s0}) q_0 (1 - q_0) \Delta V_q}{q_0 D_{i0} + (1 - q_0) D_{s0}} , \tag{14}$$

where ΔH_i, ΔV_i, ΔH_s, and ΔV_s are defined similar to ΔH and ΔV, except that the derivatives are with D_{i0} and D_{s0}, $\Delta H_q = \partial \ln[(1 - q_0)/q_0]/\partial(1/RT)$ and $\Delta V_q = \partial \Delta G_q/\partial P$. Under the assumption $q_0 D_{i0} \gg (1 - q_0) D_{s0}$, Eqs. (13) and (14) reduce to

$$\Delta H = \Delta H_i + (1 - q_0) \Delta H_q$$

and $\tag{15}$

$$\Delta V = \Delta V_i + (1 - q_0) \Delta V_q .$$

For the rapidly diffusing impurities in Pb the measured activation energies and volumes from Eq. (15) depend strongly on ΔH_q and ΔV_q, and it is therefore understandable why they may not be

characteristic of interstitial diffusion.

Since there are not sufficient experimental data to allow for the terms in Eq. (11) to be separated, some approximation will have to be made in order to proceed further with the analysis. Two assumptions will be made: (1) It will be assumed that all diffusivities are proportional to the inverse of the square root of their masses, and (2) the mass-normalized diffusivities for both interstitial and substitutional defects will be assumed independent of the impurity atom. Thus $D_{ir} = (m/m_r)^{1/2} D_{i0}$ and $D_{sr} = (m/m_r)^{1/2} D_{s0}$, where m_r is the reference mass and D_{ir} and D_{sr} are the interstitial and substitutional diffusivities which are assumed independent of the impurity. The first approximation seems somewhat palatable from simple physical arguments concerning the mass dependence of frequency factors. The second approximation which assumes that interstitial and substitutional diffusivities are independent of the defect certainly cannot be true in general. There is some evidence, however, to suggest that the second approximation may be appropriate for the diffusion of some impurities in Pb. Decker *et al.* found that the binding energy between Au-Au, Au-Ag, and Au-Pd dimers are equal for the diffusion of Au in Pb(Au), Pd(Ag), and Pb(Pd) alloys.[9] This says that diffusing Au atoms are unable to differentiate between an encounter with another Au, Ag, or Pd atom, which certainly supports the second assumption. One can also argue that chemically similar impurities should have similar values of q_0 and hence their diffusivity ratios should be proportional to the inverse ratios of the roots of their masses. This is very nearly true for Pd and Pt (Ref. 17) and for Cd and Hg (Ref. 16) in Pb. The second assumption appears on the surface to be a gross oversimplification; however, it may not be so. The expected interstitial diffusivity for each impurity species is larger than the corresponding substitutional diffusivity by a factor of about $1/c_v \sim 10^4$, where c_v is the vacancy concentration. If the differences in the interstitial and substitutional diffusivities between impurity species are much smaller than $1/c_v$, then the approximations are quite reasonable and the results should be meaningful.

A universal equation involving the equilibrium fraction q_0, the mass m of the diffusing impurity, along with D_{ir} and D_{sr} is obtained from Eq. (11) using the two assumptions:

$$D_0 = [q_0 D_{ir} + (1 - q_0) D_{sr}](m_r/m)^{1/2} . \tag{16}$$

Equation (16) was simultaneously fitted to all of the temperature and pressure impurity diffusivity data for Ni, Pd, Pt, Cu, Ag, Au, Zn, Cd, and Hg in Pb.[1-17] It was assumed in fitting Eq. (16)

that D_{sr} corresponded to Pb self-diffusion, with $q_0 = 0$, and m_r the atomic mass of Pb. Therefore, D_{sr} was first fitted to all of the temperature and pressure data for self-diffusion[18-22] and then used as a known parameter in fitting the impurity data. The frequency factors ν_{ir} and ν_{sr} which occur in the diffusivities D_{ir} and D_{sr} were corrected to first order in the temperature and pressure using Taylor series expansions for $\ln\nu_{ir}$ and $\ln\nu_{sr}$. The parameters in the fit for D_{ir}, D_{sr}, and ΔG_q included a pre-exponential or entropy term, an activation enthalpy, an activation volume, along with a temperature and pressure coefficient for the activation volume.[8] The fit was made simultaneously to 327 diffusivity measurements over a wide range of temperatures and pressures for the nine impurities. Figure 3 shows a typical fit to Eq. (16) for the atmospheric pressure data for Au and Sn in Pb. This data ranges from 60 to 300 °C for Au and 243 °C to near the melting point for Sn and illustrates that the difference between a true Arrhenius curve and Eq. (16) can be almost imperceptible. The fit was excellent over the entire range of temperature and pressure with (chi squared)/(degrees of freedom) = 0.71. The zero-pressure data generally fit within 2–3% for each diffusion couple over the entire temperature range and the high-pressure data fit was about as good
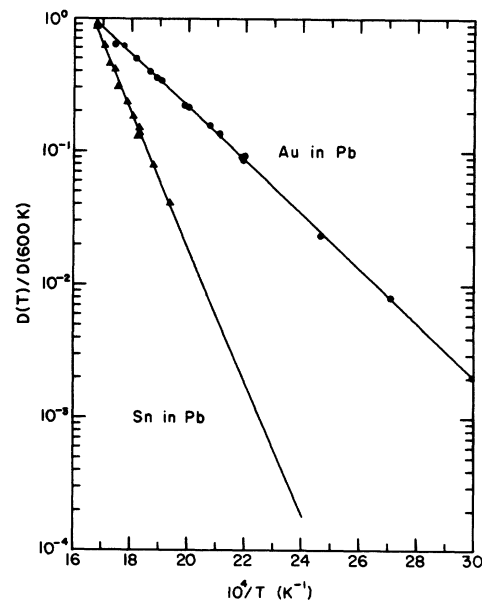

FIG. 3. The relative diffusivity data from Refs. 9 and 23 are shown versus $10^4/T$ for Au and Sn in Pb. The solid lines are fits to Eq. (16) using the parameters from Table II. The Au data (●) extend over the temperature range 60–300 °C and the Sn data (▲) 242–325 °C. The Sn solid curve was extended to illustrate along with the Au curve the linearity of the non-Arrhenius form of Eq. (16).

as the data. The results as shown in Table II are interesting and show a number of correlations. It can be seen that within the experimental error, at the reference temperature $T_0 = 600$ K and for $P = 0$, the q_0 values for the impurity groups Ni and Zn, Pd, Pt, and Au, and Cd and Hg are equal. This suggests that within each of the three groups the differences in diffusivities are primarily the result of their differing masses, whereas the differences between groups is the result of the interstitial-substitutional energy-state difference ΔG_q.

The activation volume ΔV_q can be interpreted as the difference in the lattice volume as an impurity moves from an interstitial position to a substitutional position. Hence taking these volume differences one can write $\Delta V_q = \Delta V_i^f - \Delta V_{vr} + \Delta V_{sP}$ where ΔV_i^f is the interstitial formation volume or the increase in the lattice volume which results from inserting an interstitial impurity into the lattice, ΔV_{sP} is the change in volume which results from replacing a substitutional impurity with a regular Pb atom, and ΔV_{vr} is the volume of relaxation about a free vacancy. This vacancy relaxation volume using the parameters from Table II can be approximated by $\Delta V_{vr} = V_0 - \Delta V_s + \Delta V_i = 0.34 V_0$, where V_0 is the atomic volume of Pb. If one assumes that ΔV_{sP} is small, one finds that the interstitial formation volumes ΔV_i^f range from $0.29 V_0$ for Pd, to $0.60 V_0$ for Ag, to $0.76 V_0$ for Hg in Pb. These values seem completely reasonable considering the openness of the Pb lattice and the large interstices.

Decker, Weiss, and Vanfleet[23] measured the activation volume for Sn in Pb primarily because they were sure that it was a substitutional diffuser and that the activation volume would correspond to Pb self-diffusion. The calculated value of q_0 amounted to only 20 ppm; however, the measured activation volume of $0.52 V_0$ was much too small to correspond to substitutional diffusion and seemed very mysterious. The activation volume for Sn in Pb from Eq. (14) reduces approximately to $0.4(\Delta V_i + \Delta V_q) + 0.6\Delta V_s$ which one can see includes only a 60% contribution from the substitutional activation volume ΔV_s. The point of the illustration is that because D_{i0}/D_{s0} is so large it requires that q_0 be less than about one part per million interstitial impurity concentration before the behavior really approaches the pure substitutional behavior. A number of interesting conclusions are a direct result of the ratio $D_{i0}/D_{s0} = 33\,000$ being so large. In the case of Cd and Ag diffusion in Pb 92% and 99.8% goes by the interstitial mechanism, respectively. The calculations of ΔH and ΔV from Eqs. (13) and (14) match the experimental values for the diffusion[12,17] of Cu, Ag, Au, Pd, Pt, Zn, Cd, and Hg in Pb to less than

3%. The values for Ni and Sn fit to within 10% which are all well within the experimental error considering the uncertainties in the q_0's.

ISOTOPE EFFECT

The very small values of $f\Delta K$ for the isotope effect for Cd, Ag, and Cu now have a slightly different interpretation if Eq. (11) is assumed to be the correct representation for the diffusivity. Starting with the definition for the isotope effect

$$f\Delta K = \frac{D_\alpha/D_\beta - 1}{(m_\beta/m_\alpha)^{1/2} - 1}, \tag{17}$$

and substituting Eq. (11) into Eq. (17) for two different isotopic masses, one obtains the following expression for the isotope effect:

$$f\Delta K = \frac{q_0 D_{i0}(f\Delta K)_i + (1 - q_0)D_{s0}(f\Delta K)_s}{q_0 D_{i0} + (1 - q_0)D_{s0}}$$
$$- \frac{(D_{i0} - D_{s0})q_0(1 - q_0)[\Delta G_q(\alpha) - \Delta G_q(\beta)]}{(q_0 D_{i0} + (1 - q_0)D_{s0})[1 - (m_\alpha/m_\beta)^{1/2}]RT}, \tag{18}$$

where $(f\Delta K)_i$ and $(f\Delta K)_s$ are the isotope effects for pure interstitial and substitutional diffusion. It has been assumed that Δq_0 is small and can be treated as a differential and that $\Delta G_q(\alpha)$ and $\Delta G_q(\beta)$ are the substitutional-interstitial energy-state differences for the isotopic masses α and β, respectively. In the event that interstitial diffusion predominates, Eq. (18) reduces to

$$f\Delta K = (f\Delta K)_i - \frac{(1 - q_0)[\Delta G_q(\alpha) - \Delta G_q(\beta)]}{RT[1 - (m_\alpha/m_\beta)^{1/2}]}. \tag{19}$$

As an example of the use of Eqs. (18) and (19) one might ask what energy-state difference is needed for the two isotopes to explain the measured $f\Delta K$ = 0.12, 0.25, 0.23, for Cd, Ag, and Cu in Pb, respectively.[6,29,32] Assuming that $(f\Delta K)_i$ takes on its maximum value of 1.0 then $\Delta G_q(\alpha) - \Delta G_q(\beta)$ = 28, 21, and 32 cal/mole for Cd, Ag, and Cu. These tiny energy differences which are of the order of 10^{-3} eV seem completely plausible and have been investigated in terms of a 5-frequency Einstein model, which is consistent with the enhancement theory approximations. It is predicted from Eq. (19) that the isotope effect for all of the fast diffusers in Pb will yield small values for $f\Delta K$ and it is conceivable that some of these values may even be negative. The predicted value of $f\Delta K$ for Sn in Pb, using the value of 20 ppm from Table II for q_0 and assuming the isotopic energy difference is similar to that for Cd or Ag, which have about the same mass, gives $f\Delta K = 0.55 \pm 0.05$. As was found with the analysis for the activation volume, in order to obtain a value of $f\Delta K$ which

TABLE II. q theory parameters evaluated at 600 K, $D_{tr}/D_{sr} = 33\,000 \pm 9100$. Parameters for substitutional[a] and interstitial[b] diffusivities listed below.

Impurity	$\Delta S_q/R$	ΔH_q (kcal/mole)	$\Delta V_q/V_0$	$\frac{10^4}{V_0}\frac{\partial \Delta V}{\partial T}$ (K⁻¹)	$\frac{10^3}{V_0}\frac{\partial \Delta V_q}{\partial P}$ (kbar⁻¹)	q_0	ΔG_q (kcal/mole)
Cu	1.38 ± 0.21	2.37 ± 0.23	0.121 ± 0.013	1.86 ± 0.82	−7.55 ± 1.14	0.35 ± 0.09	0.72 ± 0.49
Au	0.81 ± 0.07	3.04 ± 0.07	0.224 ± 0.010	−1.06 ± 0.32	−1.82 ± 0.52	0.15 ± 0.04	2.07 ± 0.38
Pt	1.64 ± 0.28	4.04 ± 0.30				0.15 ± 0.04	2.09 ± 0.38
Pd	0.03 ± 0.32	2.18 ± 0.32	−0.054 ± 0.014	1.58 ± 0.52	0.54 ± 0.76	0.14 ± 0.04	2.14 ± 0.36
Ni	0.61 ± 0.59	4.27 ± 0.64	0.039 ± 0.018	1.34 ± 0.75	−2.86 ± 0.72	0.049 ± 0.014	3.55 ± 0.36
Zn	1.12 ± 0.19	5.10 ± 0.19	0.130 ± 0.008	0.00	−1.00 ± 0.33	0.045 ± 0.012	3.65 ± 0.34
Ag	2.36 ± 0.08	8.01 ± 0.01	0.257 ± 0.010	−2.26 ± 0.44	0.17 ± 0.69	0.013 ± 0.004	5.19 ± 0.33
Hg	5.87 ± 0.16	16.41 ± 0.17	0.418 ± 0.008	0.42 ± 0.31	−1.92 ± 0.44	371 ± 102 ppm	9.42 ± 0.34
Cd	4.30 ± 0.18	14.62 ± 0.18	0.198 ± 0.014	2.04 ± 0.61	5.07 ± 0.96	349 ± 97 ppm	9.49 ± 0.33
Sn	1.95 ± 1.52	15.20 ± 1.69	0.252 ± 0.062	−10.7 ± 4.3	15.5 ± 4.9	20 ppm	12.88
Tl	2.05	15.44				19 ppm	13.00
Na	4.37	19.55				6 ppm	14.35

[a] $D_{sr}(o) = 1.00 \pm 0.19$ cm²/sec, $\Delta H_s = 25.71 \pm 0.20$ kcal/mole, $\Delta V_s/V_0 = 0.747 \pm 0.015$, $\frac{10^4}{V_0}\frac{\partial \Delta V_s}{\partial T} = 7.47 \pm 1.09$ K⁻¹, $\frac{10^3}{V_0}\frac{\partial \Delta V_s}{\partial P} = -8.66 \pm 1.54$ kbar⁻¹.

[b] $D_{tr}(o) = 0.0035 \pm 0.0011$ cm²/sec, $\Delta H_i = 6.55 \pm 0.45$ kcal/mole, $\Delta V_i/V_0 = 0.086 \pm 0.015$, $\frac{10^4}{V_0}\frac{\partial \Delta V_i}{\partial T} = -0.65 \pm 0.23$ K⁻¹, $\frac{10^3}{V_0}\frac{\partial \Delta V_i}{\partial P} = 2.56 \pm 0.52$ kbar⁻¹.

corresponds closely to that for substitutional diffusion, the value for q_0 needs to be of the order of 1 ppm.

CONCLUSIONS

A model is proposed which involves only substitutional, interstitial, and doublet defects which appears to be consistent with all of the diffusion data for Pb. Enhancement of both impurity and self-diffusion is interpreted in terms of the localized enhancement which occurs in the vicinity of the singlet and doublet defects. Impurity de-enhancement effects occur as the result of the attraction between interstitial and substitutional defects, with the subsequent formation of doublets, and the resultant removal of the rapidly diffusing interstitials from contributing to the diffusion process. The enhancement–de-enhancement of impurity diffusion depends on two factors: (1) the impurity concentration dependence of the diffusivity, and (2) the relative fraction of singlet and doublet impurities which can diffuse.

Impurity diffusion into pure Pb using extremely small impurity concentrations reduces to a two-mechanism model involving only substitutional and interstitial impurity defects. The doublet fraction in this case approaches zero, whereas the interstitial and substitutional impurity fractions remain finite. The wide variation in the measured activation energies and volumes for systems which seem to be dominated by an interstitial diffusion mechanism has been quite puzzling. However, the interstitial contribution to the activation energy and volume as seen from Eqs. (13) and (14) and Table II is not very large. This tends to make these values seem much more reasonable. The small activation volume of $0.52\,V_0$ for the diffusion of Sn in Pb coupled with its characteristic substitutional activation energy of 23 kcal/mole was nicely explained by Eq. (14) and the approximations of Table II.

The small measured values of $f\Delta K$ of 0.12, 0.25, and 0.23 for the isotope effect for Cd, Ag, and Cu in Pb, respectively, is interpreted in terms of a very small energy change of about 2×10^{-4} eV per atomic mass unit for the substitutional to interstitial energy state. This represents an energy-state difference of only 0.05% per atomic mass unit for the ^{109}Cd-^{115}Cd measurement. Small isotope effect measurements in the past have always been interpreted in terms of a highly correlated motion of the diffusing defect or a small value of ΔK. The arguments have not always been convincing. Furthermore, many of the small isotope effect measurements have been observed in systems where a double mechanism involving inter-

stitial and substitutional diffusion may be taking place.

The fact that the interstitial to substitutional diffusivity ratio is large, about 33 000, implies that pure substitutional diffusion behavior can be observed only if the interstitial fraction q_0 is less than a few ppm. For interstitial impurity fractions larger than this, the measured parameters such as the activation energy, activation volume, and the isotope effect depend strongly on $\Delta G_q(T, P, m)$. This Gibbs free energy is the energy needed to form a free interstitial and a free vacancy from a substitutional defect, and is extremely important

in interpreting any type of diffusion measurement where the interstitial substitutional mechanism is applicable. The measured diffusivity ratio $D_{io}/D_{so} = 3.3 \times 10^4$ is consistent with its approximated value of $1/c_v$.

ACKNOWLEDGMENT

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