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Diffusion of Cadmium in Lead

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The diffusivity D_2 of cadmium in high-purity lead single crystals has been measured from 150°C to the melting point, using tracer and sectioning techniques, and is described by $D_2=0.409\exp(-21\,230/RT)$ cm^2/sec. Lead self-diffusivity is enhanced by the addition of cadmium in accordance with $D_1=D_1^0\times(1+b_1X+b_2X^2+b_3X^3)$, where b_i are the linear and higher-order enhancement factors, and D_1^0 and D_1 are the self-diffusivity of lead in pure lead and in lead alloys containing X atom fraction of cadmium, respectively. It is found that $b_1\cong D_2/D_1^0$, varying from 19 to 45 over the temperature range 300–198°C. It is shown from the results of Howard and Manning that the minimum linear enhancement factor for the vacancy mechanism is $b_{\min}=-18+1.9448(D_2/D_1^0)$, substantially larger than that observed. The fast diffusion of cadmium cannot then be accounted for on the basis of the model proposed by Lidiard for the simple vacancy mechanism. It is suggested that cadmium, like the solutes Ag, Au, and Cu, dissolves both interstitially and substitutionally in lead, the enhancement of lead self-diffusion being associated with an interaction between vacancies and interstitial cadmium ions. A comparison of diffusion data for several impurities in lead shows that the dominant mechanism of solute diffusion is determined primarily by solute valence. Since the dominant diffusion mechanism of a solute is a natural consequence of its degree of interstitial dissolution, it is proposed that solute valence plays a major role in determining the energetics of interstitial dissolution.

I. INTRODUCTION

THE diffusivities of mercury, cadmium, magnesium, silver, and gold in lead were measured by Seith and his co-workers.[1,2] Their findings showed that all of these solutes have very large diffusivities, ranging from two to five orders of magnitude greater than lead self-diffusion. Dyson *et al.*[3] have more recently measured the diffusion of copper in lead, and have found its diffusivity to be even greater than any of the aforementioned. Recent tracer diffusion studies by Kidson[4] and Dyson *et al.*[3] have served to confirm and refine quantitatively the very rapid diffusion of gold and silver in lead.

There is convincing evidence that the solutes copper, gold, and silver are at least partially dissolved in the interstices of lead, and diffuse primarily by the interstitial mechanism.[3,4] The possibility of dislocations acting as short-circuiting paths for diffusion has been effectively ruled out. In considering the interstitial dissolution of such solutes in lead, it is significant that the octahedral interstitial sites bounded by the quadruply ionized lead ions are sufficiently large, of radius 1.62 Å,[3] to accomodate any of the above solute ions.

It is of great importance to recognize that small additions of a fast diffusing substitutional solute, diffusing by a vacancy mechanism, actually necessitate an enhancement of the self-diffusion. Hoffman, Turnbull, and Hart[5] first showed that if the solute in a dilute binary alloy is substitutionally dissolved and diffuses by a vacancy mechanism at a faster rate than the solvent, there results an enhancement of the self-diffusion which is linear in the solute concentration. Such a linear enhancement may be described by

$$D_1/D_1^0=1+bX. \tag{1}$$

This effect of added solute arises from nearest-neighbor solute-vacancy interactions, which can enhance or suppress the total equilibrium fraction of vacancies in a crystal, and from solute-solvent interactions which result in changes in neighboring solvent-vacancy exchange frequencies. Such changes in jump frequencies lead also to a complex interdependency of solute and solvent correlation factors for vacancy diffusion in the dilute alloy.

Lidiard[6] has calculated the factor b for a dilute fcc alloy, based on such a model, allowing for changes in vacancy jump frequencies occurring within nearest neighbor distance of an impurity atom or an impurity-vacancy pair. More recently, Howard and Manning[7] have performed the calculations for this model in greater generality by calculating the correlation factor for solvent diffusion in detail. These calculations show that corresponding values of b and D_2/D_1^0 specify the locus of all possible sets of the three jump frequency ratios w_4/w_0, w_3/w_1, and w_2/w_1. The notation of Howard and Manning[7] is used for the jump frequencies w_i.

Separate investigations by Seith and Keil[2] and by Dyson *et al.*[3] have shown no observable enhancement of lead self-diffusion in the presence of gold and silver solutes, so that the rapid rate of solute diffusion cannot be attributed to a vacancy mechanism. Since the interstitial diffusion of a small addition of solute is not expected to have any first-order effect on the separate vacancy mechanism of self-diffusion, the absence of an enhancement effect lends great support to the interstitial dissolution of the noble metal solutes in lead.

The rapid diffusion of cadmium in lead measured by Seith *et al.*,[1] the small size of the cadmium ion (ionic

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[1] W. Seith, E. Hofer, and H. Etzold, Z. Elektrochem. **40**, 322 (1934).

[2] W. Seith and A. Keil, Z. Physik. Chem. **B22**, 350 (1933).

[3] B. F. Dyson, T. Anthony, and D. Turnbull, J. Appl. Phys. **37**, 2370 (1966).

[4] G. V. Kidson, Phil. Mag. **13**, 247 (1966).

[5] R. E. Hoffman, D. Turnbull, and E. W. Hart, Acta Met. **3**, 417 (1955).

[6] A. B. Lidiard, Phil. Mag. **5**, 1171 (1960).

[7] R. E. Howard and J. R. Manning, Phys. Rev. **154**, 561 (1967).

radius[8] of 0.97 Å) and the convincing evidence that the noble metal solutes diffuse in lead by the interstitial mechanism provide ample reason for investigating the mechanism of diffusion and the character of dissolution of cadmium in lead. It is also of interest to understand the importance of the valence difference between solvent and solute as it affects the character of dissolution in polyvalent metals. An extensive experimental study has therefore been made of both the diffusion of cadmium in pure lead and of the effect of cadmium solute additions on lead self-diffusion. In addition, an examination of certain theoretical aspects of the self-diffusion enhancement effect has yielded results which are relevant to the interpretation of such diffusion data.

II. EXPERIMENTAL TECHNIQUE

Lead single crystals were grown from the melt, using 99.9999% pure lead. Attempts to grow lead-rich cadmium alloys by the same technique were unsuccessful since most of the cadmium solute was lost by evaporation. It was instead found possible to cast Cd-Pb alloys in evacuated and sealed Pyrex tubes, and to obtain in this way a significant length of single crystal in each cast alloy. All crystals were subsequently annealed for two to three days at 260°C.

Single-crystal samples for diffusion were cut from these crystals by a spark-cutting technique. The surface of each sample to be electroplated was microtomed flat within about 0.5 μ. Immediately before electroplating, this surface was polished gently with a small dry swab of soft cotton to remove any surface oxide film.

Small amounts of the Cd^{115m} and Pb^{210} isotope solutions, as received from Nuclear Science and Engineering Corporation of Pittsburgh, Pennsylvania, were added to separate dilute cyanide baths, which were then used to electroplate a thickness of 1–2 μ of metallic Cd^{115m} or Pb^{210} onto the single exposed flat face of each sample. Since formation of an oxide layer at the tracer-sample interface can easily arrest or impede the process of diffusion into the sample, as noted by Dyson *et al.*,[3] it is necessary to perfect surface preparation and deposition techniques which avoid such oxide formation. Successful deposition of cadmium tracer without subsequent hold-up effects was obtained by use of a modified electroplating solution. Ammonium hydroxide was used in lieu of sodium hydroxide, and the *p*H adjusted to about 10.5.

Electroplated samples were then sealed in evacuated Pyrex tubes, and diffusion anneals conducted in furnaces whose temperatures were maintained constant within ±1°C. Temperatures were measured at frequent intervals during the anneals using calibrated thermocouples.

To avoid evaporation of cadmium from the alloy sample surfaces during the diffusion anneal, it was found necessary to include within the same evacuated tube many small slices of the same alloy. This procedure effected a preferential evaporation from the large surface area of these slices to establish equilibrium with the vapor.

Another important experimental procedure was adopted in order to assure the greatest possible accuracy of the enhancement effect measurements $D_1(X_i,T_j)/D_1^0(0,T_j)$ for several solute concentrations X_i at each fixed temperature T_j. Pb^{210} was diffused simultaneously into a pure lead sample and many alloy samples of compositions X_i, which were placed very close together within the same furnace, and for the same total diffusion time t. In this way, each of these samples was assured an identical diffusion anneal and an identical average temperature T_j, so that more meaningful values of the ratios $D_1(X_i,T_j)/D_1^0(0,T_j)$ were obtained. To avoid vapor transport of cadmium solute, it was, of course, necessary to enclose each sample of different composition within a separate small capsule.

After the diffusion anneal, samples were quenched to room temperature and all sides perpendicular to the active face were sectioned off with a microtome, or etched with an acetic acid and peroxide solution, in order to remove any effects due to surface diffusion.

The final cross-sectional area of each specimen was measured both before and after final sectioning. After levelling the active face of each sample with respect to the plane of motion of the microtome blade, at least 50 slices were cut from each sample, individually weighed on a Mettler semimicro balance, and finally counted.

The activity of Cd^{115m} in each slice of a cadmium diffusion sample was counted by means of a thin end-window flow-type Geiger counter with standardized geometry. The activity of Pb^{210} may not be reliably inferred by measurements of β radiation from the Bi^{210} daughter, with the assumption that secular equilibrium has been attained after six half-lives of Bi^{210} decay. It was determined that the faster diffusion of Bi^{210} in fact results in a relative deficiency of Bi^{210} near the surface, where restoration of secular equilibrium then depends upon the very slow decay of Pb^{210}. It is instead possible to measure the Pb^{210} 0.047 MeV γ radiation directly. After dissolving each slice in acetic acid, the Pb^{210} activity was measured in a well-type γ spectrometer.

Slice thicknesses were calculated from the measured slice weights, the measured cross-sectional areas, the known density of pure lead, 11.3437 g/cm^3, and the variation of lead density with additions of cadmium as determined by Jenckel and Mäder.[9] Alloy samples were subjected to chemical analysis after diffusion anneals, the results of which agreed well with the nominal atomic percent cadmium added when casting the alloys. Specific activities were calculated from the measured total activity of each slice, the average background counts and the weight of each slice.

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[8] L. Pauling, *Nature of the Chemical Bond* (Cornell University Press, Ithaca, N. Y., 1945), p. 346.

[9] E. Jenckel and H. Mäder, Metallwirtschaft **16**, 499 (1937).

III. THEORY

It may be shown directly from the results of Howard and Manning[7] that for a given ratio D_2/D_1^0, only values of b greater than a certain minimum value b_{min} are compatible with solute diffusion by the vacancy mechanism. This minimum enhancement effect occurs for the case of solute atoms tightly bound to vacancies, i.e., in the notation of Howard and Manning, when $w_3/w_1 \rightarrow 0$, and also in the limit that $w_4/w_0 \rightarrow 0$ and $w_2/w_1 \rightarrow \infty$, so that only w_1 jumps contribute to the enhancement effect. Taking these limits and substituting the appropriate limiting value of the correlation factor for w_1 jumps in the alloy $\chi_1 = 0.4862$, as calculated by Compaan and Haven,[10] we obtain

$$b_{\text{min}} = -18 + 4\chi_1(D_2/D_1^0) = -18 + 1.9448(D_2/D_1^0). \quad (2)$$

This special case of minimum enhancement is indeed a very extreme one, and is likely to be physically unrealizable. Existing sets of experimental data for b and D_2/D_1^0 for many solutes in fcc metals fit the model extremely well, yielding physically reasonable values of the jump frequency ratios. In fact, the observed enhancement factors b are in all cases very much greater than b_{min}.

It is of particular interest that the data of Resing and Nachtrieb[11] for the solute thallium in lead fit the model very well, and thus are in agreement with the vacancy mechanism of solute diffusion. The excellent fit of many sets of experimental data to the model is convincing evidence that the model represents accurately the physics of the enhancement effect, and that the minimum b value [Eq. (2)] derived from the model represents the minimum physically possible enhancement effect compatible with solute diffusion by a simple vacancy mechanism.

The theory for linear enhancement applies only to small impurity concentrations, less than 1 or 2 at.%, and most experimental investigations do show that higher-order enhancement effects occur at higher concentrations. Many investigators have fitted such high concentration data to an exponential form which was derived by Overhauser[12]:

$$D_1/D_1^0 = e^{bX}. \quad (3)$$

On the basis of the Lidiard model, however, such a form is not justifiable. The essential physics of this model in fact suggest that since the interaction of single-solute atoms with solvent atoms and vacancies gives rise to a linear enhancement, the occurrence of solute atom pairs, which will have an entirely different interaction with solvent atoms and vacancies, should give rise to an additional enhancement of self-diffusion varying as b_2X^2. The inclusion of such effects into the Lidiard model is, of course, much more tedious, and the resultant solution for b_2 is more complex, but is of the same general form as b_1. The magnitude of b_2 at any given temperature then depends upon the energetics of the solute-solute interaction and the interaction of such a pair with adjacent solvent atoms and vacancies, as well as in a complex way upon the many jump frequencies and correlation factors involved in the motion of solvent atoms near such pairs. It follows that the magnitude of the factor b_2, and hence of all higher-order factors b_n as well, will have a unique value for any temperature T, although displaying a complex temperature dependency through the various jump frequencies. The enhancement effect should therefore be described more generally by

$$D_1/D_1^0 = 1 + b_1X + b_2X^2 + b_3X^3 + \cdots. \quad (4)$$

If higher-order enhancement effects are evident in experimental data, it is then important to fit the data to the more rigorous form of (4), and thereby obtain a more physically meaningful value of the linear enhancement factor b_1.

IV. RESULTS

The specific activity, representative of tracer concentration, was found to obey a Gaussian distribution, which agrees with the appropriate solution of the diffusion equation for a finite source at the planar surface of a semi-infinite medium, providing the source is depleted in a time which is very short compared with the total diffusion time[4]:

$$C(x,t) = [S/(\pi Dt)^{1/2}]e^{-x^2/4Dt}. \quad (5)$$

Here S is the total amount of tracer deposited on the plane face of the material and C is the final concentration of tracer at a distance x from the planar surface after a diffusion anneal time t. The diffusion constant D is easily obtained by a least-squares linear solution of the plot of the logarithm of the specific activity (the logarithm of the concentration) versus x^2. A typical penetration plot of this kind is shown by a solid line in Fig. 1.

Occasionally the initial point of such a plot was a little above the least-squares solution, indicating a slight hold-up of diffusion due to oxidation at the surface. Whenever such oxide hold-up occurred to a greater extent than this, many initial points resembled an error function in form, and the data were considered unreliable. At low temperatures, penetration plots sometimes displayed non-Gaussian behavior at deep penetrations. The dashed line in Fig. 1 is the only penetration plot for cadmium diffusion which showed such an effect. Such diffusion "tails" were indicative of some mode of diffusion faster than normal volume diffusion, but these tails occurred only after a significant regime of Gaussian behavior, and at low tracer concentrations. These high initial points and diffusion tails were automatically

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[10] K. Compaan and Y. Haven, Trans. Faraday Soc. **52**, 786 (1956).

[11] H. A. Resing and N. H. Nachtrieb, J. Phys. Chem. Solids **21**, 40 (1961).

[12] A. W. Overhauser, Phys. Rev. **90**, 313 (1953).

eliminated from consideration during computer solution by a specialized least-squares analysis. All plots were strictly Gaussian over a range of one to three decades of tracer concentration, including from 20–75 data points.

As is expected for volume diffusion by a unique mechanism, a plot of the logarithms of calculated D_i's versus the reciprocal of absolute temperature is quite linear, both for cadmium diffusion in pure lead, and for lead self-diffusion. These data are shown in Fig. 2. Single-crystal samples were used for all diffusion experiments in pure lead, so that no effects due to grain boundary diffusion are present. A few polycrystalline alloy samples were used in the enhancement effect experiments, but only at high temperatures, and the diffusion constants determined from these samples showed no deviation from the trend of results from single-crystal alloy samples.

A simple calculation reveals that it is unreasonable to suppose that the fast diffusion of cadmium in lead is a result of short-circuiting diffusion paths such as dislocations. At a depth of about $3(Dt)^{1/2}$ into the sample, the number of diffused tracer atoms in a 1-cm^2 section one atom high is estimated from the specific activity to be about 4×10^9. This is far too high a tracer concentration to be accomodated by the 10^6 or 10^7 dislocation cores one might expect in a well-annealed lead sample. In addition, certain pure lead and alloy single crystals were annealed for much longer times. Volume-diffusion coefficients determined using samples from these crystals were in all cases in good agreement with all other data, indicating that the dislocation content of all single crystals was sufficiently small that the Gaussian profiles were indeed representative of volume diffusion only. It is nevertheless possible that the diffusion tails mentioned above are the result of dislocation diffusion deep in the specimen, since the number of tracer atoms estimated to lie in a similar section located at the point of departure to such a tail is somewhat higher than 10^7.

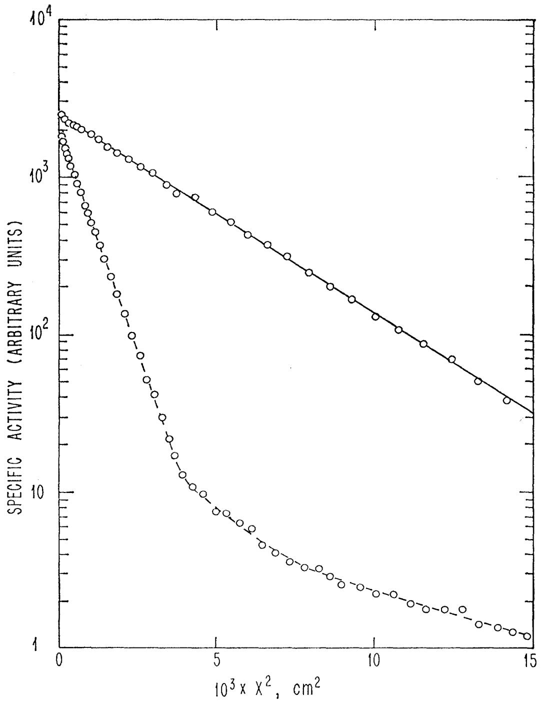

FIG. 1. Diffusion penetration curves obtained by diffusing Cd^{115m} into pure lead. Data on the solid line show the Gaussian penetration typical of normal volume diffusion in the absence of a hold-up effect or a diffusion "tail," while data on the dashed line show the diffusion "tail" obtained for cadmium diffusion at 150°C.

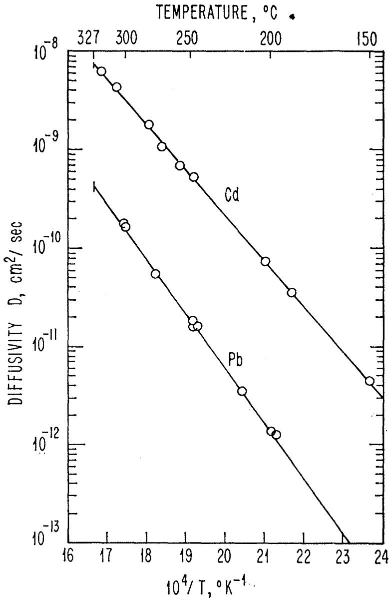

FIG. 2. Diffusivity of cadmium and lead in lead.

The diffusion constant of cadmium diffusion in lead was determined by least-squares analysis to be

$$
\begin{aligned}
D_2 &= D_{20}\exp(-Q_2/RT),\\
D_{20} &= 0.409\pm0.1\ \text{cm}^2/\text{sec}, \qquad (6)\\
Q_2 &= 21.23\pm0.20\ \text{kcal/mole}.
\end{aligned}
$$

Although the self-diffusion of Pb^{210} into pure lead samples was performed primarily as a reliable reference to calculate the enhancement effect data, the experiments were conducted over a wide temperature range and were sufficiently reproducible to make worthwhile a least-squares solution for the self-diffusion constant in pure lead:

$$
\begin{aligned}
D_1^0 &= D_{10}\exp(-Q_1/RT),\\
D_{10} &= 0.887\pm0.3\ \text{cm}^2/\text{sec}, \qquad (7)\\
Q_1 &= 25.52\pm0.30\ \text{kcal/mole}.
\end{aligned}
$$

These least-squares solutions are shown as solid lines in Fig. 2. It is important to note that cadmium diffuses at a rate ranging from about 20–100 times faster than lead itself over the temperature range investigated. This ratio of diffusivities is much higher than that for any other solute in an fcc metal which is believed to diffuse by a vacancy mechanism.

The cadmium diffusivities measured by Seith *et al.*[1] were somewhat greater than those measured in this investigation. Since Seith used nonradioactive alloy couples and spectrographic analysis in making this study, higher cadmium concentrations were necessary than are needed in tracer impurity diffusion studies. Thus Seith's results are more representative of cadmium diffusion in a dilute lead-cadmium alloy than of that in pure lead, suggesting that cadmium diffusion in lead is also enhanced by additions of cadmium. A preliminary experiment has shown that this is so, and that the enhancement effect is of the right magnitude to explain Seith's results. The lead self-diffusivity measurements agree quite well with previous determinations by Hudson and Hoffman[13] and by Resing and Nachtrieb.[10] In fact, the agreement between these measurements and those of Resing and Nachtrieb is such that a least-squares analysis of both these sets of data may be more meaningful than the two independent results. Such an analysis gives the following result:

$$\begin{aligned} D_1^0 &= D_{10} \exp(-Q_1/RT), \\ D_{10} &= 0.995 \pm 0.2\ \mathrm{cm^2/sec}, \qquad (8) \\ Q_1 &= 25.65 \pm 0.25\ \mathrm{kcal/mole}. \end{aligned}$$

Initial enhancement-effect experiments carried out at five fixed temperatures demonstrated that there was indeed an acceleration of lead self-diffusion with additions of cadmium, and that the effect was primarily of higher order than linear for solute concentrations above 2 at.%. It was then necessary to obtain much more complete data over the entire range of the effect. Such data have been obtained for three temperatures, and do indeed fit the form of Eq. (4).

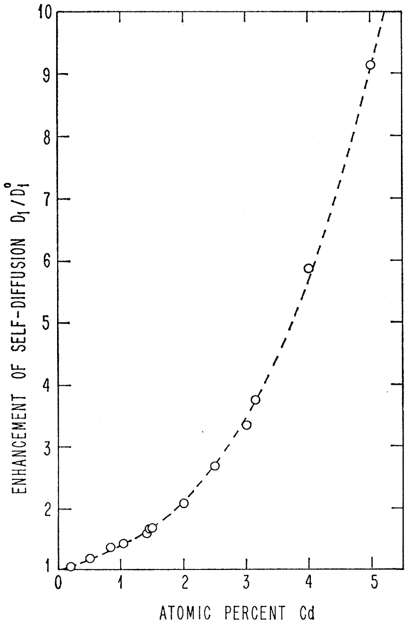

FIG. 3. Enhancement of lead self-diffusion by additions of cadmium at 248.2°C. The least-squares solution for linear and higher-order coefficients is shown as a dashed line.

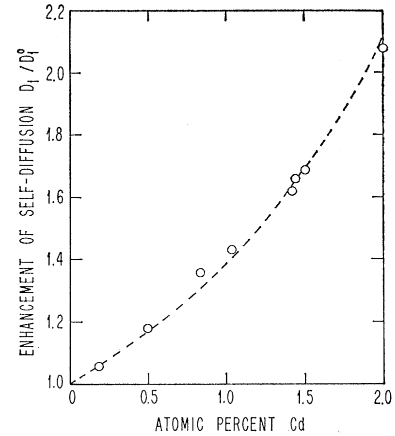

FIG. 4. Enhancement of lead self-diffusion by very small additions of cadmium at 248.2°C. The least-squares solution is again shown as a dashed line.

The full range of the enhancement effect is shown in Fig. 3 for the temperature of maximum solubility of cadmium in lead, 248°C. The low-concentration regime of these data is shown on an expanded scale in Fig. 4. It was possible to calculate statistically significant values for the coefficients b_1, b_2, and b_3 from this data. The solution obtained is plotted as a dashed line in Figs. 3 and 4. For two other temperatures, 300 and 199°C, statistically significant values of the coefficients b_1 and b_2 were obtained. The results of these calculations, as well as corresponding values of b_{min}, the minimum linear-enhancement factor for a vacancy mechanism of solute diffusion, are given in Table I. It is seen that the observed linear-enhancement factors are distinctly less than the corresponding values b_{min}. An upper bound for b_1 may be calculated by performing a strictly linear least-squares analysis of the low-concentration data at each temperature. At the lowest temperature, even such an upper bound of the linear enhancement factor is clearly less than the corresponding value of b_{min}.

The least-squares calculation of the coefficients b_i was

TABLE I. Lead self-diffusion enhancement factors b_i for cadmium solute, at several temperatures. The observed linear enhancement factors b_1 are to be compared with the corresponding values of b_{min}, the minimum linear enhancement factor for a vacancy mechanism, and of the diffusivity ratios D_2/D_1^0, which are also tabulated.

T (°C)	D_2/D_1^0	b_{min}	b_1	b_2	b_3
198.7	44.907	69.34	45.197	438.1	···
248.2	29.073	38.54	30.028	407.7	44 286
300.5	19.924	20.75	19.138	1070.2	···

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[13] J. B. Hudson and R. E. Hoffman, Trans. Met. Soc. AIME **221**, 761 (1961).

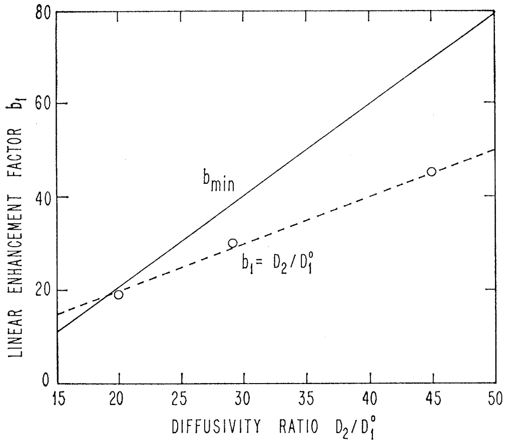

FIG. 5. Comparison of the observed linear enhancements and the minimum possible enhancement by a simple vacancy mechanism of solute diffusion.

performed by computer matrix analysis, in conjunction with an appropriate significance test. All data were weighted equally. Data initially taken at intermediate temperatures are in good qualitative agreement with the other data, but there are not sufficient data to allow a least-squares solution for both b_1 and b_2.

Figure 5 illustrates clearly that the experimentally determined linear-enhancement coefficients b_1 are considerably less than the minimum b_{min} for a normal vacancy mechanism of solute diffusion. Both are plotted as a function of the experimentally determined diffusivity ratio D_2/D_1^0. The value of b_{min} is shown as a solid line, while a dashed line $b_1=D_2/D_1^0$ indicates that within the limits of experimental error

$$b_1(\mathrm{Cd/Pb})=1.0(D_2/D_1^0). \qquad (9)$$

V. DISCUSSION

Most solutes in fcc metals are believed to diffuse by a vacancy mechanism. The Lidiard model for solute-enhanced self-diffusion has confirmed this belief in almost every case by showing remarkable agreement with measurements of solute diffusion, enhanced self-diffusion, and even of correlation factors.[14] The diffusion rate of cadmium impurity in lead relative to that of self-diffusion, however, is much faster than that of other solutes believed to be dissolved substitutionally and diffusing by a vacancy mechanism. Moreover, the linear enhancement effect of cadmium solute on lead self-diffusion is much too small to be explained on the basis of a vacancy mechanism of solute diffusion. This is demonstrated very clearly in Fig. 5. It is thus concluded that cadmium solute does not diffuse in lead by a simple vacancy mechanism.

The evidence for interstitial dissolution and diffusion of other small solute ions in lead suggests that cadmium may also dissolve at least partly in the interstices of lead. In this case, however, despite the fast rate of solute diffusion, there is a definite linear enhancement of self-diffusion. The presence of this effect rules out the possibility of solute diffusion by a strictly interstitial mechanism.

The fact that $b_1=D_2/D_1^0$ attests to a unique relation between the mechanism of solute diffusion and the enhancement effect. This relation also suggests, however unlikely, the possibility of the simple interchange mechanism, for which $b_1=f_0(D_2/D_1^0)$, where $f_0=0.7815$ is the correlation factor for self-diffusion in a pure fcc crystal. Although one cannot rule out this possibility altogether, it is difficult to envision a good physical reason for the very strong higher-order enhancement effects if this mechanism were operative.

Thus each of three alternative mechanisms considered thus far, the vacancy, interstitial, and simple interchange, has been rejected as a possible explanation of the diffusion of cadmium in lead. Since interstitial formation is quite likely, the dissociative mechanism of Frank and Turnbull,[15] which involves an equilibrium between substitutional and interstitial solute atoms, will be considered in greater detail. This alternative is very attractive since fast solute diffusion and a small enhancement of self-diffusion are very easily explained by the fast diffusion of the interstitial solute and a slower vacancy diffusion of substitutional solute. Making the assumption that the diffusion of substitutional and interstitial species proceed independently by the vacancy and interstitial mechanisms, the effective diffusion constant may be written

$$D_{\mathrm{eff}}=D_iX_i+D_sX_s, \qquad (10)$$

where X_i and X_s are the respective equilibrium fractions of the total solute concentration X in the interstitial and substitutional states. Cadmium diffuses at a rate which is two orders of magnitude slower than silver in lead, which strongly suggests that if a fraction of cadmium solute is diffusing independently by the interstitial mechanism, X_i is certain to be very small. Considering also that the enhancement factor b_1 and the diffusivity ratio D_2/D_1^0 are of the same magnitude, it is most likely that $D_iX_i \simeq D_sX_s$. Since the temperature variation of both D_iX_i and D_sX_s should be characterized by unique and very different exponents, the Arrhenius plot of $D_2=D_{\mathrm{eff}}$ versus $1/T$ would show a distinct curvature, such as is observed for many solutes in bcc metals.

Instead, the data show that the diffusion constant of cadmium in lead has a unique activation energy, and thus, most probably, a unique mechanism of diffusion, at least over the temperature range investigated. It should then be considered that the interstitial and substitutional species do not diffuse independently, as described by Eq. (10). An attractive interaction between interstitial solute ions and vacancies will result in

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[14] S. J. Rothman and N. L. Peterson, Phys. Rev. **154**, 552 (1967).

[15] F. C. Frank and D. Turnbull, Phys. Rev. **104**, 617 (1956).

correlated interstitial migration as well as a linear enhancement of the self-diffusion. Such an interaction may indeed explain the close relation between the kinetics of solute diffusion and the observed enhancement of self-diffusion, $b_1 = D_2/D_1^0$. It is therefore proposed that cadmium dissolves in lead by the dissociative mechanism, and that interstitial cadmium ions interact with vacancies during the diffusion process in such a way that a fast mode of solute diffusion occurs in conjunction with a relatively small linear enhancement of self-diffusion. The detailed theory for such a mechanism of solute diffusion, and further experimental verification of this proposal are to be published at a later date.

The diffusivities of silver,[3] cadmium, and thallium[11] in lead demonstrate the striking effect of solute valence on the rate of diffusion in lead:

$$D_{\mathrm{Ag}}(+1) \gg D_{\mathrm{Cd}}(+2) \gg D_{\mathrm{Tl}}(+3) > D_{\mathrm{Pb}}^0. \quad (11)$$

The respective valences have been indicated in parentheses. This correlation supports the view that such solutes dissolve as ions, giving up their respective number of valence electrons to the conduction band of the host metal. The screening theory for the role of solute valence in diffusion by a normal vacancy mechanism was developed by Lazarus.[16]

The self-diffusion enhancement-effect data for additions of these solutes to lead are evidence that silver diffuses interstitially, that cadmium diffuses by a mechanism involving the correlated motion of interstitials and vacancies, and that thallium diffuses by a normal vacancy mechanism. Solute diffusion occurs primarily by the interstitial mechanism only if the fraction of interstitial solute X_i is sufficiently large, and by a normal vacancy mechanism only if X_i is negligible. It is thus evident that the interstitial character of dissolution varies markedly with the ionic charge Z of the solute.

The effective charge introduced into the crystal by an interstitial impurity is simply $Z_{\mathrm{eff}} = Z_{\mathrm{solute}}$, whereas that for a substitutional impurity is $Z_{\mathrm{eff}} = Z_{\mathrm{solute}} - Z_{\mathrm{solvent}}$. The localization of conduction electrons to screen the charge of an impurity ion is a function of this effective charge. The energy associated with this localization of electrons must then be quite different for interstitial and substitutional states of the same solute. The effective charge of silver solute is least in the interstitial site, whereas that of thallium is least in the substitutional site. It is inferred that a lesser effective charge in the interstitial site leads to a lowering of the free energy of this site relative to that of the substitutional site. This may be understood on the basis of free-electron screening if the electron kinetic energy dominates exchange effects. It then follows that interstitial dissolution will be most favored for singly valent solutes in lead, and will be less favored as the solute valence is increased.

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[16] D. Lazarus, Phys. Rev. 93, 973 (1954).