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Enhancement of Lead Self-Diffusivity by Gold and Silver Additions

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It has been proposed that noble-metal solutes diffuse in lead primarily by the interstitial mechanism, while cadmium solute diffuses by means of tightly bound interstitial-vacancy pairs. It is reasoned that noble-metal interstitial ions should also interact attractively with lead vacancies and result in a small enhancement of the self-diffusivity with solute additions. Consequently, lead self-diffusivity has been measured as a function of small gold- and silver-solute additions. The linear enhancement factors determined from these measurements are most consistent with the interpretation that noble-metal solutes diffuse primarily by the interstitial mechanism and that the relatively small enhancements of lead self-diffusion are due to attractively bound interstitial-vacancy pairs.

I. INTRODUCTION

It has been shown[1] that additions of a substitutional impurity diffusing by the vacancy mechanism enhance the self-diffusivity in a dilute fcc alloy such that

$$D_1(X_2) \gtrsim D_1^0\left[1+(b_{11})_{\min} X_2\right] , \tag{1}$$

$$(b_{11})_{\min} = -18 + 1.9448(D_2^0/D_1^0) . \tag{2}$$

This minimum enhancement condition is derived from the Lidiard model for the linear enhancement of self-diffusion,[2] as refined by Howard and Manning,[3] for the case of tightly bound impurity-vacancy pairs. D_1^0 and $D_1(X_2)$ are the self-diffusivities in pure solvent and in an alloy containing solute atom fraction X_2, respectively, D_2^0 is the impurity diffusivity, and $(b_{11})_{\min}$ is the minimum linear enhancement factor for the vacancy mechanism. Equations (1) and (2) show that additions of a rapidly diffusing impurity result in a large linear enhancement of the self-diffusivity, providing that the impurity diffuses by the vacancy mechanism.

Dyson, Anthony, and Turnbull[4] recognized that the extreme rapidity of copper, gold,[5] and silver diffusion in lead by the vacancy mechanism necessitates a large enhancement of the lead self-diffusivity with solute additions, despite the very small solid solubilities. On finding no measurable enhancement of the lead diffusivity with additions of copper and gold, it was proposed[4] that the solutes copper, gold, and silver diffuse primarily by the interstitial mechanism, dissolving at least partially in the interstices of lead. It was considered that solute diffusion by the interstitial mechanism proceeds independently of solvent diffusion by the vacancy mechanism. It was further proposed that these solutes dissolve in lead by the dissociative mechanism, i.e., both substitutionally and interstitially, as first proposed by Frank and Turnbull[6] to explain the diffusion of copper in germanium.

Experimental studies of the fast diffusion of cadmium in lead[1] point out a similar inconsistency with impurity diffusion by the vacancy mechanism. The linear enhancement factor b_{11}, although positive, is significantly less than $(b_{11})_{\min}$. It was proposed[1,7,8] that cadmium also dissolves by the dissociative mechanism, but that the positively charged interstitial cadmium ions bind strongly to the effective negative charge of nearest-neighbor vacancies. The resultant interstitial solute-vacancy pair defect is considered[7] the logical intermediate defect state of the dissociative mechanism. A kinetic model for the diffusion of solute and solvent in a dilute dissociative alloy,[7] patterned after the Lidiard model for the substitutional alloy,[2] showed that tightly bound interstitial solute-vacancy pairs diffuse in such a manner that $b_{11} \lesssim f_0(D_2^0/D_1^0)$, where $f_0 = 0.78146$ is the correlation factor for vacancy self-duffusion in a pure fcc solid, and that the solute correlation factor f_2 becomes very small. Since it had been observed that $b_{11} \simeq (D_2^0/D_1^0) \simeq f_0(D_2^0/D_1^0)$, within experimental error, for additions of cadmium to lead, the isotope effect for diffusion of cadmium in lead was then measured as a further test of the proposed mechanism. This measurement[8] showed that $f_2 \simeq 0.09$, in direct agreement with the theoretical prediction.

On the basis of the screened electrostatic interaction model developed by Lazarus,[9] it is expected[7] that an interstitial divalent cadmium ion interacts more strongly with vacancies than interstitial monovalent noble-metal ions. For this reason, it is envisioned[7] that the fraction χ_p of interstitial cadmium-vacancy pairs is much greater than the fraction χ_i of free cadmium interstitials, so that the diffusion of both solute and solvent in the alloy is determined by the migration of these close pairs. In the case of the noble-metal solutes, however, the fraction of interstitial-vacancy pairs relative to the fraction of free interstitials may be significantly reduced so that solute diffusion is dominated by migration of free interstitial solute atoms.

If the interstitial noble-metal ions do associate with vacancies, albeit to a lesser extent than the divalent cadmium ion, the assumption that the migration of interstitial solute proceeds independently of the vacancy diffusion of solvent is not strictly correct. Let us therefore consider the effect of interstitial-vacancy pairs on both solute and self-diffusivities in dilute noble-metal–lead alloys. It is likely that interstitial noble-metal solute-vacancy pairs diffuse in much the same manner as interstitial cadmium-vacancy pairs, so that we may postulate a characteristic diffusion constant D_p, composed of the average solute jump frequency multiplied by the effective correlation factor[7] for these jumps, for this mechanism of diffusion. The effective solute diffusion constant in this dissociative alloy should then be expressed

$$(D_2^0)_{\rm eff} = \chi_s D_s + \chi_p D_p + \chi_i D_i \quad . \tag{3}$$

Here, χ_s, χ_p, and χ_i are the respective fractions of the total solute concentration X_2 in the substitutional, interstitial-vacancy pair and free interstitial solute states, while D_s, D_p, and D_i are the respective characteristic diffusion constants of these solute species. Since interstitial jump frequencies are considered to be very large compared to vacancy jump frequencies, and the migration of free interstitials in uncorrelated, it is expected that $D_i \gg D_p$, D_s. If χ_i is sufficiently large with respect to χ_p and χ_s that $\chi_i D_i \gg \chi_p D_p$, $\chi_s D_s$, the effective solute diffusion constant will be determined entirely by the interstitial contribution

$$(D_2^0)_{\rm eff} \simeq \chi_i D_i \quad , \tag{4}$$

as is believed to be the case for noble-metal diffusion in lead.[4,10]

Noble-metal solute diffusivities in lead agree very well with this expectation, first of all because of the extreme rapidity of their diffusion. Second, the Arrhenius parameters D_0 and Q derived from the temperature dependence of the diffusion are very characteristic of those for interstitial diffusion. Third, the lack of any observable curvature in the Arrhenius plot of $\log_{10} D$ versus $1/T$ indicates that only one mechanism of diffusion is making a significant contribution to the total solute diffusion constant.

Considering only linear contributions to the enhancement of self-diffusion, the solvent diffusion constant in noble-metal–lead alloys may be written

$$D_1(X_2) = D_1^0 \left[1 + (b_{11})_s X_2 + (b_{11})_p X_2\right] \quad . \tag{5}$$

Here, $(b_{11})_s$ is the linear enhancement factor arising from the diffusion of substitutional solute atoms by the vacancy mechanism, while $(b_{11})_p$ is that arising from diffusion of close pairs. Since it is considered that substitutional solute-vacancy interactions are very small in lead,[7,8] we anticipate that $(b_{11})_s$ will have a value similar to that for the solute thallium in lead,[11] i.e., of the order of unity. Considering the limited solid solubilities, it is easily reasoned that such a small contribution to the enhancement will not be measurable. If a measurable linear enhancement of the self-diffusivity results from additions of noble-metal solutes, the effect may thus be attributed to the attractive interaction of interstitial solute ions with vacancies, and to the resultant migration of close pair defects, i.e., $b_{11} \simeq (b_{11})_p$.

Since other investigators[4,12] have measured lead self-diffusivity in copper-lead, gold-lead, and silver-lead alloys and obtained diffusion constants agreeing well with the known values of lead self-diffusivity, it is suspected that the enhancement effect due to migration of close pairs is quite small. Nevertheless, since the observation of a positive enhancement effect might demonstrate the presence of these proposed interstitial-vacancy defects in the noble-metal–lead alloys, three experiments were carried out to determine the enhancement effect of gold and silver solutes.

II. EXPERIMENTAL PROCEDURE

Gold and silver were decided upon as solutes because of their greater solid solubility in lead. The solubility of Au in Pb at 200 °C is reported to be 0.08 at.%,[13] and is expected to be somewhat greater at 215 °C, the eutectic temperature. The maximum solubility of Ag in Pb is reported as 0.19 at.% at 300–304 °C.[13] Single crystals of pure lead (nominally 99.9999% pure), lead + 0.02 at.% Au, lead + 0.04 at.% Au, lead + 0.065 at.% Au, lead + 0.08 at.% Au, lead + 0.09 at.% Ag, and lead + 0.18 at.% Ag were prepared by the same methods used to obtain single crystals of cadmium-lead alloys.[1] The preparation of diffusion samples, electroplating of Pb^{210} isotope, and diffusion anneals were carried out in the same manner as for determination of the diffusion enhancement effect in Cd-Pb, also fully reported in Ref. 1. Errors due to separate determination of time and temperature for separate diffusion anneals were avoided by diffusing Pb^{210} into a sample of pure lead and alloys of several solute compositions simultaneously, within the same furnace and for the same total time t. This procedure permits a much greater accuracy in the values obtained for $D_1(X_2)/D_1^0$ than can be obtained for values of the diffusion constant itself.

The vapor pressures of both gold and silver are low enough at the temperatures of diffusion anneal, so that vapor transport of solute between alloys of different composition is insignificant during the time of anneal. Electroplated samples of pure lead, Pb + 0.04 at.% Au, and Pb + 0.08 at.% Au were sealed in the same evacuated Pyrex tube and annealed for approximately 72 days at 199.4 °C. Electroplated samples of pure Pb, Pb + 0.09 at.% Ag, and Pb + 0.18 at.% Ag were sealed together in another evacuated Pyrex tube and annealed for three days at 300.3 °C.

A third enhancement effect experiment was performed in order to demonstrate the linearity of the effect more conclusively for gold solute additions, and to show the lack of dependence of the effect on higher dislocation densities introduced by microtoming of the surface to be electroplated. Two samples, of compositions Pb + 0.04 at.% Au and Pb + 0.08 at.% Au, were subjected to a two day anneal at 215 °C to further reduce dislocation density, and chemically etched, in lieu of microtoming, just prior to electroplating the lead tracer. These two samples, together with microtomed and electroplated samples of pure Pb, Pb + 0.02 at.% Au, Pb + 0.04 at.% Au, Pb + 0.065 at.% Au, and Pb + 0.08 at.% Au, were sealed together in an evacuated Pyrex tube and annealed for six days at 215.2 °C.

Samples were arranged within each tube so that any temperature gradient along the length of the tube, during the anneal, would result in a systematic scatter of the results. Temperature within each furnace was measured by means of a thermocouple directly adjacent to the Pyrex capsule, and no temperature gradient was detectable along the length of the capsules. Temperatures were measured frequently during the anneals, and were maintained within less than ± 1 °C of the desired temperatures.

The samples were quenched to room temperature immediately after removal from the furnace. Sectioning, weighing of slices, and the counting procedures were carried out as described in Ref. 1 for the measurement of lead self-diffusivity in cadmium-lead alloys. The remainder of each diffusion sample was then chemically analyzed for gold or silver content by Arnold Greene Laboratories of Natick, Mass. Results of these chemical analyses, which agreed closely with the nominal alloy concentrations, were utilized in further analysis of the results.

III. RESULTS

The diffusion penetration profiles, plots of $\log_{10}(\mathrm{Pb}^{210}$ specific activity) versus the square of the penetration distance x^2, for diffusion of Pb^{210} into pure lead and the noble-metal–lead alloys of each enhancement effect experiment are shown in Figs. 1, 2, and 3. The linearity of these plots attests to the Gaussian concentration dependence expected for the experimental boundary conditions[5]:

$$C(x,t) \propto (Dt)^{-1/2} \exp(-x^2/4Dt) \quad . \tag{6}$$

The compositions indicated in these figures are those determined by chemical analysis. Since the lead self-diffusivity in each specimen is inversely proportional to the slope of these plots, it is immediately evident that the self-diffusivity is measurably enhanced by additions of gold and silver.

Error analysis and least-squares calculation of the diffusivities were performed as described by Wolberg.[14] Estimates of the errors in measurement of sample diameter, slice weight, and tracer activity were used to calculate estimated standard deviations of both ordinate and abscissa values for each data point of the penetration profiles. Lead self-diffusivities were then calculated by a weighted least-squares method of solution, the weights being determined by the estimated standard deviations of both ordinate and abscissa. Counting statistics alone were not sufficient to account for the experimentally observed standard deviations of ordinate values, as was also found from a statistical analysis of data for an isotope effect determination.[8] Inclusion of an additional counting error of 0.2–0.5 %, attributable to counter instability and/or count-

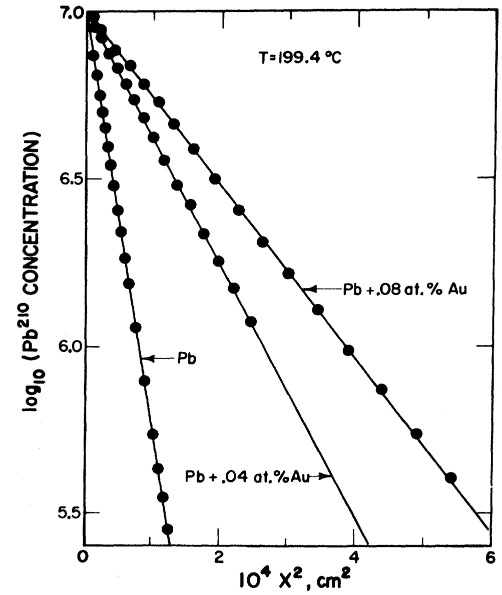

FIG. 1. Penetration profiles for lead self-diffusion in pure lead and gold-lead alloys, at 199.4 °C. The linear least-squares solutions are shown as solid lines. For clarity of presentation, the log intercepts have been adjusted to the same value.

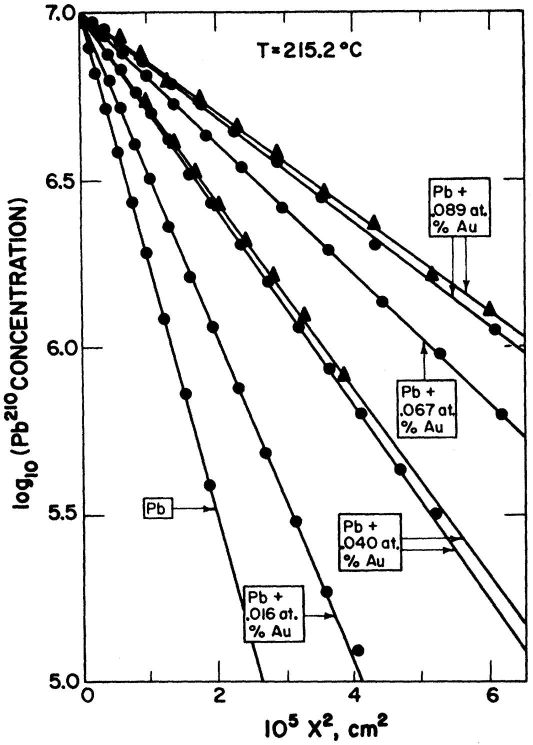

FIG. 2. Penetration profiles for lead self-diffusion in pure lead and gold-lead alloys, at 215.2 °C. The triangular data points are determined from alloy samples which were specially annealed and etched, in lieu of microtoming, prior to deposition of tracer. The solid lines represent the linear least-squares solutions. For clarity of presentation, the log intercepts have been adjusted to the same value.

rate dependence, reduces the resultant values of χ^2 to credible values, i.e., values for which the associated probabilities are greater than 5%. The additional counting error in measurement of the isotope effect[8] was approximately 0.1–0.2%, but further effort had been made, of necessity, to reduce such error. The calculated diffusivities are quite insensitive to the weighting procedure since the experimental errors are very small, and are apparently well estimated. The resulting values for lead self-diffusivity in pure lead agree well with the results of previous investigations.[1,11,15] A reliable estimate of the standard deviation of the calculated diffusivities also results from use of this weighted least-squares analysis.

The data points representing the first slices from the surfaces of those samples annealed at 215.2 °C were somewhat above the line determined by the remainder of points for these samples. These points were rejected in the final least-squares calculations and are not shown in Fig. 2. It is believed that this surface holdup of tracer activity is due to a surface oxidation, as previously explained.[1]

The linear enhancement effect may be expressed

$$L(X_2)=D_1(X_2)/D_1^0-1=b_{11}X_2\ , \qquad (7)$$

and solved by the least-squares method accordingly. The estimated standard deviations of the diffusivities are used to calculate estimated standard deviations of the linear enhancement effect $L(X_2)$, and the error in measurement of X_2 is estimated. These values are represented by the error bars in Figs. 4, 5, and 6, which show the enhancement effect as a function of solute atom fraction X_2 for the three experiments. The calculated values of b_{11} and their estimated standard deviations are also included in these figures.

It was at first thought that the nonlinearity of the enhancement effect for gold additions at 199.4 °C (Fig. 4) was due to experimental error. However, Rossolimo,[16] in the course of other experimental work concerning the gold-lead alloy, has determined that the solid solubility of gold in lead at 200 °C is 0.066 at.%. The enhancement effect in the Pb + 0.08 at.% Au alloy was thus determined above the solubility limit. The enhancement effect should be very linear up to the solubility limit for solute additions of this small magnitude. Since additions of solute beyond the solubility limit remain in precipitated form, no further enhancement should occur with such additions. Assuming then that the effect is linear, which is demonstrated by the results of the 215.2 °C experiment (Fig. 5), the linear enhance-

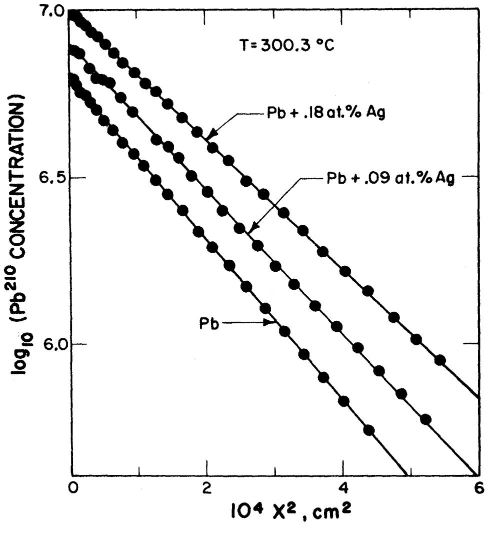

FIG. 3. Penetration profiles for lead self-diffusion in pure lead and silver-lead alloys, at 300.3 °C. The linear least-squares solutions are shown as solid lines. The log intercepts have been adjusted to slightly separated values for clarity of presentation.

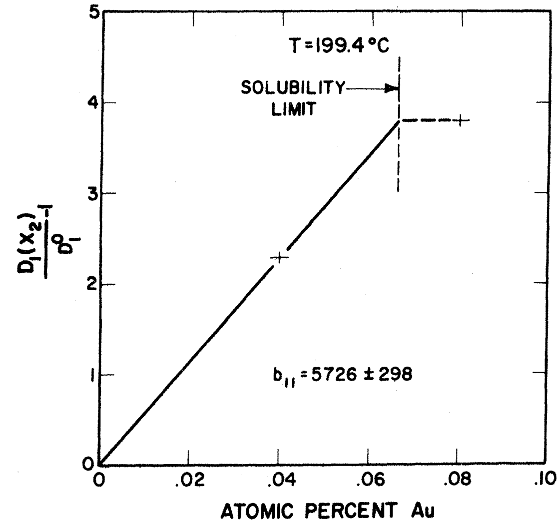

FIG. 4. The enhancement of lead self-diffusivity by additions of gold solute, at 199.4 °C. It was ascertained that the addition of 0.08 at. % Au exceeded the solubility limit, and that the solubility limit could be determined from the results as shown in the figure.

TABLE I. The experimentally determined values of the linear enhancement factors b_{11} and the impurity to self-diffusivity ratios D_2^0/D_1^0 are listed for the alloy systems and temperatures of this investigation. Also listed are the minimum linear enhancement factors $(b_{11})_{\min}$ consistent with the vacancy mechanism of solute diffusion, deduced from the values of D_2^0, and the maximum impurity to self-diffusivity ratios $(D_2^0/D_1^0)_{\max}$ consistent with vacancy diffusion, as deduced from the values b_{11}.

Alloy system	T (°C)	D_2^0/D_1^0	$(b_{11})_{\min}$	b_{11}	$(D_2^0/D_1^0)_{\min}$
Au-Pb	199.4	152 946	297 431	5726	2953.5
Au-Pb	215.2	89 152	173 365	4312	2226.5
Ag-Pb	300.3	870.7	1675.3	136.8	79.60

ment factor may be calculated from the single data point below the solubility limit. In addition, the solubility limit may be calculated from the results, as is graphically demonstrated in Fig. 4. The resultant value for the solubility limit of gold in lead at 199.4 °C is 0.066± 0.004 at.%, in excellent accord with Rossolimo's result.

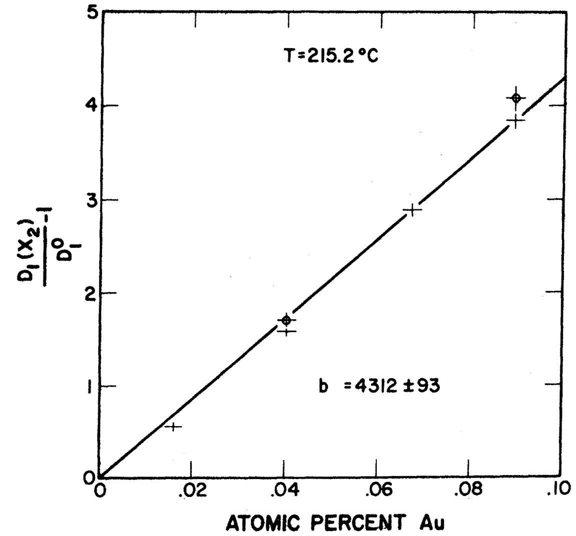

FIG. 5. The enhancement of lead self-diffusivity by additions of gold solute, at 215.2 °C. The circled data points were determined from samples which were specially annealed and etched, in lieu of microtoming, prior to deposition of tracer.

IV. DISCUSSION

In Table I are listed several experimental and calculated results for the alloy systems and temperatures of these experiments. The results of Dyson, Anthony, and Turnbull[4] and Kidson[5] have been used for the diffusivities D_2^0 of silver and gold, respectively, and the combined results of Miller[1] and Resing and Nachtrieb[11] have been used for the lead self-diffusivity D_1^0. The values of b_{11} are those determined by this series of experiments.

If gold and silver dissolve substitutionally and

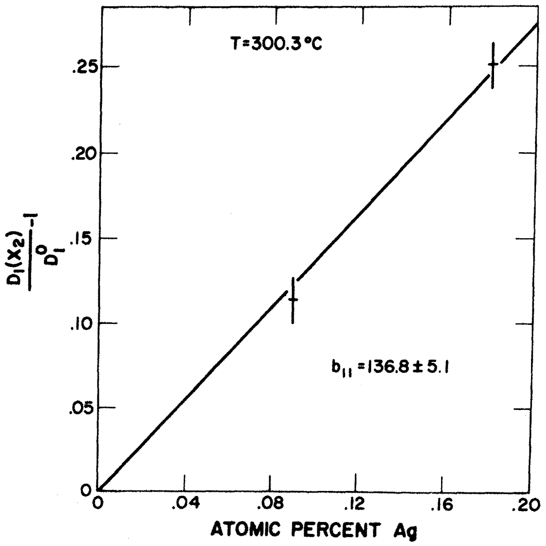

FIG. 6. The enhancement of lead self-diffusivity by additions of silver solute, at 300.3 °C.

diffuse with the observed diffusivities D_2^0 by the vacancy mechanism, the linear enhancement of the self-diffusivity must be equal to or greater than that described by $(b_{11})_{\mathrm{min}}$[Eq. (2)]; these values are also listed in Table I. It is seen that the observed linear enhancement factors b_{11} are in all cases an order of magnitude less than $(b_{11})_{\mathrm{min}}$, so that the kinetics of solute and self-diffusion in these alloys are clearly inconsistent with the assumption that these solutes diffuse primarily by the vacancy mechanism. It is similarly possible to calculate the maximum value of D_2^0/D_1^0 consistent with the vacancy mechanism of impurity diffusion and the observed linear enhancement effect from the relationship of Eq. (2); these values of $(D_2^0/D_1^0)_{\mathrm{max}}$ are also listed. Comparison of these values with the observed values of D_2^0/D_1^0 again confirms the conclusion of Dyson, Anthony, and Turnbull[4] that vacancy diffusion of gold and silver in lead does not make a significant contribution to the total solute diffusivity. It is therefore considered that the dominant contribution to gold and silver diffusivity in lead arises from other than simple vacancy diffusion.

Other possible volume diffusion mechanisms for a substitutionally dissolved solute are the simple interchange and ring mechanisms, for which $b_{11} = f_0(D_2^0/D_1^0)$ and $b_{11} > f_0(D_2^0/D_1^0)$, respectively. By comparing the observed values of b_{11} and D_2^0/D_1^0 in Table I, it is seen that in all cases $b_{11} \ll D_2^0/D_1^0$, $f_0(D_2^0/D_1^0)$. We may therefore rule out the possibility of these solute diffusion mechanisms also.

For the case of a fast diffusing substitutional impurity, no other known or proposed volume diffusion mechanism results in a lesser enhancement of the self-diffusion than the simple interchange mechanism. We may conclude that if the solute is dissolved entirely in substitutional sites, the diffusion does not occur by a volume mechanism. The possibility of solute diffusion along short-circuiting paths such as dislocations must then be considered; grain boundary diffusion need not be considered since single crystals were used in all investigations.[4,5]

If diffusion occurs primarily along dislocations, the diffusivity is strongly dependent upon the density and array of dislocations. Kidson[5] demonstrated that the diffusivity of gold in lead is unaltered by the introduction of a stable dislocation array parallel to the diffusion direction, at both high and low temperatures. This result is evidence that gold diffuses primarily by means of a volume diffusion mechanism. Although a similar experiment for the diffusion of silver in lead has not been performed, the simple Arrhenius temperature dependence of the diffusivity is a strong indication that silver also diffuses by a volume mechanism. The results of the experiment for the enhancement of lead self-diffusivity by gold additions shows that the enhancement effect does not depend significantly on dislocation density. As may be seen in Fig. 5, the enhancement effect is unchanged, within experimental error, by the presence or absence of dislocations introduced by microtoming the surfaces of 0.04 and 0.08 at.% gold-lead alloys. It is believed that the small differences in the effects observed with and without microtoming of the surface are due to the much greater surface roughness, $\pm 2\mu$, of the unmicrotomed specimens. This result, as well as the linearity and reproducibility of the observed effect, is evidence that the enhancement of lead self-diffusion by noble-metal solutes is also a true volume diffusion effect. Since both the solute diffusivities and enhancement effects apparently result from volume diffusion, we must consider the alternative possibility – that these solutes are not entirely dissolved in the substitutional sites.

Dissolution by the dissociative mechanism[6] is the most general alternative to a substitutional solution. We have seen that three distinct states of dissolved solute atoms contribute to the solute diffusivity, as described by Eq. (3), while only two of these states may contribute to the linear enhancement of self-diffusion [Eq. (5)]. We may interpret the fast diffusivity as resulting from diffusion of free interstitial solute atoms by the interstitial mechanism, as proposed by Dyson, Anthony, and Turnbull,[4] but the enhancement effect indicates that either the substitutional or interstitial solute atoms are strongly attracted to vacancies.

The calculations of March and Murray[17] show that the electronic screening of the effective point charge of a substitutional impurity is nearly complete at nearest-neighbor distance in lead and other polyvalent metals. It is therefore expected that substitutional impurity-vacancy interactions are quite small in such metals as lead and aluminum. The diffusion of impurities in aluminum[18] and of thallium in lead[11] agrees with this expectation. It is therefore difficult to explain the large linear enhancement factors b_{11} for gold and silver additions to lead in terms of an expectedly small substitutional solute-vacancy interaction.

On the other hand, the effective point charge of an interstitial solute ion should not be so well screened at the nearest lattice-site distance. In addition, it is expected that the effective positive charge of a noble-metal interstitial ion should interact attractively with the negative charge of a nearest-neighbor vacancy. It is therefore proposed that the observed linear enhancements of lead diffusion by gold and silver additions are due to the association of interstitial solute ions with nearest-neighbor vacancies, while the solute diffuses primarily by the interstitial mechanism.

It is further proposed that the interstitial-vacancy pairs migrate as set forth by Ref. 7, but that the vacancy interaction of noble-metal interstitial ions is weaker than that of cadmium interstitials.[8] This is in accord with the screened electrostatic interaction model.[9] Consequently, dissociative interstitial jumps are more frequent, the fraction of free interstitials is enhanced relative to the fraction of close pairs, and the migration of free interstitials by the interstitial mechanism is the major contribution to solute diffusivity.

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[1] J. W. Miller, Phys. Rev. 181, 1095 (1969).

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

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

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

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

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

[7] J. W. Miller, Phys. Rev. 188, 1074 (1969).

[8] J. W. Miller and W. A. Edelstein, Phys. Rev. 188, 1081 (1969).

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

[10] T. R. Anthony and D. Turnbull, Appl. Phys. Letters 8, 120 (1966).

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

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

[13] M. Hansen, *Constitution of Binary Alloys* (McGraw-Hill, New York, 1958), pp. 222–224, 40–41.

[14] J. R. Wolberg, *Prediction Analysis* (Van Nostrand, Princeton, 1967), Chap. 3.

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

[16] A. Rossolimo (private communication).

[17] N. H. March and A. M. Murray, Proc. Roy. Soc. (London) A261, 119 (1961).

[18] N. L. Peterson and S. J. Rothman, Argonne National Laboratory Annual Progress Report No. ANL-7299, 1965 (unpublished).