

## Unexpectedly Small Effect of Isotopic Mass on Diffusion of Silver in Lead\*

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The effect of isotopic mass for diffusion of silver in lead was measured to test the proposal that silver diffuses primarily by a simple interstitial mechanism. The relative diffusivity of the radioisotopes  $^{105}\text{Ag}$  and  $^{110m}\text{Ag}$  was accurately measured by codiffusion into single crystals of high-purity lead, sectioning, and analyzing the  $\gamma$  radiation from each section. The value of the effect  $E$  determined from the results of three separate experiments close to  $300^\circ\text{C}$  is  $0.25 \pm 0.05$ . Alloying of lead with 0.08-at.% Ag did not change the value of the effect within experimental error. A further experiment performed at  $150^\circ\text{C}$  yielded approximately the same result. Since the anticipated value of  $E$  for a simple interstitial mechanism is close to unity, our results indicate that the mechanism for diffusion of silver in lead is more complex than has been thought.

### I. INTRODUCTION

The migration of interstitials in crystalline materials is an important kinetic process that is not well understood. In addition to the classical interstitial systems such as carbon in iron, self-interstitials and gas-atom interstitials are currently receiving great attention. Much of this attention is due to the realization that such interstitials play an important role in determining the behavior of reactor materials during irradiation. Of fundamental importance are the atomic interactions and energetics of interstitial formation, the mechanisms by which interstitials affect many physical properties of materials, and the details of the migratory process of interstitial defects.

The basic mechanism of interstitial migration has long been thought to be the simplest example of random walk.<sup>1</sup> Recent experimental results, however, indicate that the mechanism is quite complex in many instances.<sup>2-9</sup> These results also suggest that the mechanism is similar in such apparently different solid solutions as carbon in iron<sup>6,7</sup> and the noble metals in lead or other polyvalent metals.<sup>9</sup> These metal-metal interstitial alloys are especially suitable for the fundamental investigations that may lead to greater comprehension of the mechanisms for dissolution and migration of interstitials.

The rapid diffusivity of silver, gold, and copper in lead<sup>10,11</sup> indicates that these solutes dissolve, at least partially, in the interstices of the lead lattice and diffuse primarily by an interstitial mechanism.<sup>10</sup> On the other hand, the finite enhancement of lead self-diffusivity by additions of silver and gold,<sup>9</sup> as well as the internal-friction effects observed by Turner *et al.*,<sup>4</sup> suggest that the noble-metal interstitials interact with the lead lattice in a manner which is not well understood. The present measurements of the effect of isotopic mass on diffusion should increase our understand-

ing of the physical mechanisms.

The effect of isotopic mass on diffusion,<sup>12</sup> defined as

$$E = \frac{D_\alpha/D_\beta - 1}{(m_\beta/m_\alpha)^{1/2} - 1}, \quad (1)$$

has its maximum value of unity for thermally activated diffusion of noninteracting particles by independent random walks, provided that no many-body interactions occur at the saddle point.<sup>13</sup> Here  $D_\alpha$  and  $D_\beta$  are the coefficients of diffusion for two chemically equivalent isotopes of masses  $m_\alpha$  and  $m_\beta$ . The value of the effect  $E$  is a measure of the participation of other atoms and other lattice defects in the diffusive process. If diffusion occurs primarily by a single mechanism,  $E$  may be expressed as the product of three factors:

$$E = f_c \Delta K f_n, \quad (2)$$

where

$$0 < f_c, \Delta K, f_n \leq 1. \quad (3)$$

If no other atoms or defects participate in the diffusive process, each factor is unity. However, other atoms or lattice defects generally do perturb or couple to a diffusive process. There are three recognized mechanisms by which such coupling occurs.<sup>13-16</sup> Each mechanism causes a decrease in one of the three factors.

Lattice defects may participate in the process of migration so as to cause the vectors of successive jumps of the tracer to be correlated.<sup>13</sup> Migration of the tracer is then nonrandom. Interaction of the tracer atom with other lattice defects can increase the correlativity.<sup>14</sup> The factor  $f_c$  expresses the effect of such correlation on diffusivity of the tracer, and hence on the effect of mass as well.

The kinetic factor  $\Delta K$  is less than unity if additional atoms participate dynamically in the elementary jump, provided that only the tracer atom

is relocated at the conclusion of the jump.<sup>15,16</sup>

The number factor

$$f_n = \left[ \left( \frac{(n-1)m_0 + m_\beta}{(n-1)m_0 + m_\alpha} \right)^{1/2} - 1 \right] / \left[ \left( \frac{m_\beta}{m_\alpha} \right)^{1/2} - 1 \right] \quad (4)$$

describes the decrease in the effect  $E$  that results if  $n$  atoms are relocated by the jump.<sup>17</sup> Here  $m_0$  is the mass of the additional  $(n-1)$  atoms relocated by such a jump. The proposed direct interchange and ring mechanisms are classic examples of such a participation effect.<sup>1,18</sup>

Since the simple interstitial mechanism<sup>1</sup> is an independent random walk of a single particle, both  $f_c$  and  $f_n$  should be unity for this mechanism. Although the anticipated value of  $\Delta K$  is less certain, it is close to unity for diffusion by the vacancy mechanism in close-packed structures<sup>19</sup> and some interstitial solid solutions.<sup>20,21</sup> Theory<sup>17</sup> and computer simulations<sup>22,23</sup> also predict that  $\Delta K$  should be close to unity. The value of  $E$  is thus expected to be close to unity for the simple interstitial mechanism of diffusion. The experiments described herein are a test of this model for the case of silver diffusing in lead.

## II. EXPERIMENTAL TECHNIQUE

### A. Preparation and Annealing of Samples

Lead and silver-doped lead monocrystals were grown from the melt in quartz tubes using 99.9999% pure lead and silver, obtained from Cominco American, Inc. Sections of the alloyed crystal were chemically analyzed to determine the content of silver; these results agreed well with the concentration calculated from the original charges of lead and silver. The cylindrical crystals were approximately 13, 19, and 25 mm in diameter. They were next cut normal to the cylindrical axis by the process of spark erosion to provide samples at least 7-mm thick. Immediately prior to electroplating, one of the flat surfaces of each sample was microtomed to be flat within 0.5  $\mu\text{m}$ . All other surfaces were masked with a lacquer.

The radioisotope  $^{110m}\text{Ag}$  was obtained as a 1N nitric acid solution of high specific activity from International Chemical and Nuclear Corporation. The  $^{105}\text{Ag}$  was prepared at Argonne National Laboratory by the reaction  $^{103}\text{Rh}(\alpha, 2n)^{105}\text{Ag}$ . Silver was separated from the rhodium by first dissolving the entire target in concentrated hydrochloric acid using an electrolysis.<sup>24</sup> The other electrode was graphite. The majority of the rhodium was then precipitated as  $\text{Rh}(\text{OH})_3$ . The method of anionic exchange described by Louw and Robb<sup>25</sup> was used to elute the chlorides of rhodium and silver separately from the remaining solution. This procedure was repeated several times to obtain carrier-free  $^{105}\text{Ag}$  of high specific activity, dissolved in 9N

hydrochloric acid.

Deposition of a thin layer of radiotracer and subsequent annealing of a monocrystalline specimen usually result in a dependence of concentration on depth that is Gaussian within experimental error; such a result is obtained because the solution of the partial differential equation for diffusion of a thin finite source approximates the Gaussian solution for an instantaneous source:

$$C(x) = C_0 e^{-(x^2/4Dt)}, \quad (5)$$

if the time required for dissolution of tracer is negligible compared with the time  $t$  of annealing.<sup>26</sup> Here  $C(x)$  is the concentration of tracer as a function of the depth  $x$ ,  $C_0$  is the concentration at the surface of a sample, and  $D$  is the coefficient of diffusion. Accurate measurements of coefficients of diffusion and effects of isotopic mass are possible if this Gaussian dependence is verified experimentally.

If the solubility of an impurity is sufficiently small, however, the time  $\tau$  required to dissolve a thin deposited layer can be comparable with a reasonable time of annealing.<sup>11</sup> In such a case, non-Gaussian profiles of concentration result. Since the solubility of silver in lead is small,<sup>27</sup> it is important to minimize  $\tau$  so that it is short compared to the time  $t$ . We accomplished this in accordance with Kidson's result<sup>11</sup> by adjusting the appropriate experimental parameters. We increased the surface area of the samples and the specific activity of the radiotracer. The solubility was effectively maximized, for most of the experiments, by annealing the samples close to the eutectic temperature of 304 °C. Finally, the samples were annealed for times that were more than an order of magnitude greater than the calculated times  $\tau$ .

Non-Gaussian profiles of concentration can also result if the rate of dissolution of tracer is sufficiently reduced by the rate-limiting kinetics of other interfacial processes. Such effects have been reported.<sup>28</sup> The presence of oxides at the intermetallic interface can act as a barrier to dissolution of tracer. Similarly, formation of intermetallic compounds at this interface can also reduce the rate of dissolution. We obtained such non-Gaussian profiles in our preliminary investigations and determined that the rate of dissolution of tracer was sensitive to details of the electrolytic procedure. Therefore, great efforts were expended to optimize the procedure. The best results were obtained by increasing the concentration of radiotracer relative to all other constituents of the bath. For this reason, the original isotopic solutions were neutralized by drying and redissolving, and the baths were depleted only 50–90% during electrolysis.

To make the bath, a mixture of approximately equal activities of the original solutions of  $^{105}\text{Ag}$  and  $^{110\text{m}}\text{Ag}$  was dried to a salt. This salt was redissolved in about 30 ml of distilled water. The total activity of each bath was approximately  $10^6$  dis/sec. Sodium-cyanide powder was finally added to raise the  $pH$  to about 10.5. A platinum anode was used for the electrolysis, and the dc voltage was adjusted so that the electroplating current was 30–50 mA.

Rinsing and drying the electroplated surface was also a critical operation since these procedures also influenced the rate of dissolution of tracer in the sample. Successive rinses in relatively large volumes of distilled water, acetone (to remove the lacquer), and petroleum ether were most effective in avoiding stains on the deposited layer. Samples were then individually encapsulated under vacuum in Pyrex tubes. The samples were annealed for 50–250 min, and correction for the period of heating was made using the data of Dyson *et al.*<sup>10</sup> The temperature was measured at the outer surface of the Pyrex tube with a calibrated chromel-alumel thermocouple. The difference between this temperature and the sample temperature was determined in a separate run, and appropriate correction was made. The sample temperature was known within  $0.5^\circ\text{C}$ . Samples were quenched to room temperature immediately after removal from the furnace.

#### B. Determination of Profile of Concentration

The cylindrical surface of each sample was turned down on a lathe to preclude any systematic error due to surface diffusion of radiotracer. After alignment of the sample in the microtome for cuts parallel to the original microtomed surface, the sample was sectioned from this surface to a depth such that the decrease in activity was greater than two orders of magnitude. Many microtomed slices were taken to comprise a section, and each section, 50–100  $\mu\text{m}$  in thickness, was placed in a tared vial. These sections were then dissolved, after weighing, in equal volumes of an acetic acid-hydrogen peroxide (2:1 by volume) solution. After dissolution of the lead slices, a small amount of nitric acid was added to assure dissolution of the silver.

The depth dependence of silver concentration must be known in order to determine the effect of isotopic mass. The effect is most conveniently and accurately determined if the depth dependence is Gaussian within experimental error for both isotopes.

The total  $\gamma$  activity, i. e., the sum of  $\gamma$  radiation emitted by both isotopes, was measured in a well-type NaI (Tl) counting apparatus described previously,<sup>29</sup> using the two discriminations in energy that are shown in Fig. 1 as  $L_1$  and  $L_2$ . After cor-

rection was made for dead time, the total specific activities for each discrimination were calculated as a function of the depth using the sample diameter, weights of the sections, and density of lead. The two resultant profiles of concentration for each sample were for two distinct linear combinations of the two isotopic specific activities. The isotopic diffusivities are sufficiently close that these linear combinations should be Gaussian within experimental error if the individual isotopic profiles are sufficiently Gaussian. Although some experimentally determined profiles showed slight deviations from Gaussian behavior close to the surface, the two profiles determined for each sample were Gaussian within experimental error over at least two orders of magnitude of change in the specific activity. In addition, the depth dependence of each pair of profiles was identical within experimental error. We may infer from these results that the depth dependence of concentration is Gaussian for both isotopes individually, within experimental error, over at least two orders of magnitude of change in their concentration.

Equation (5) shows that a Gaussian profile of concentration is linear if  $\log_{10} C(x)$  is plotted versus  $x^2$ . Shown in Fig. 2 are the logarithmic profiles of concentration for two of the pure lead samples annealed close to  $300^\circ\text{C}$ . The lower plot is the worst profile that we deemed acceptable for a credible measurement of the effect of isotopic mass. Dissolution of tracer in this sample was somewhat retarded, as evidenced by the departure from linearity of the data for the first few slices nearest the surface. Data from these slices were

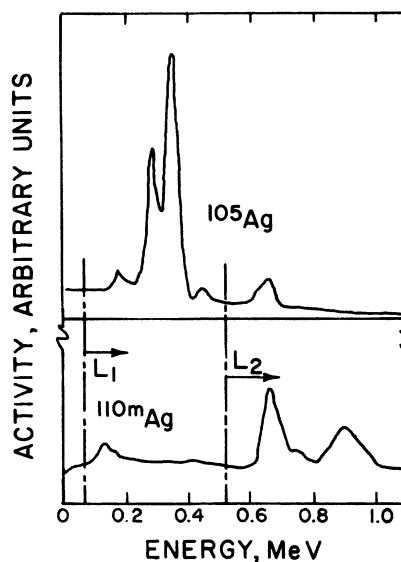


FIG. 1. Spectra of  $\gamma$  radiation for both  $^{105}\text{Ag}$  and  $^{110\text{m}}\text{Ag}$ , as measured in these experiments.

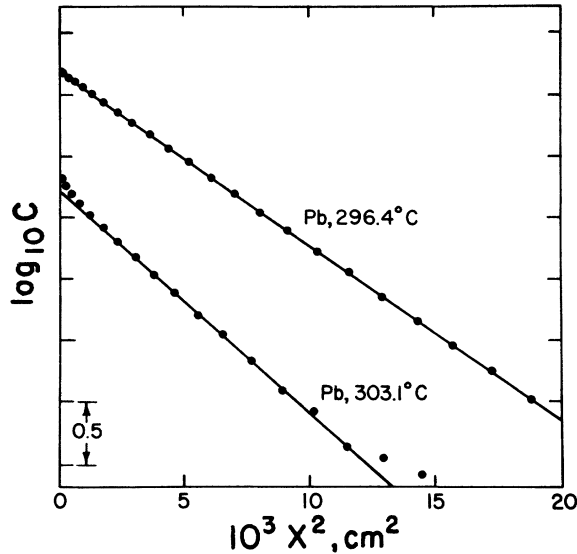


FIG. 2. Logarithmic profiles of total concentration of tracer for the codiffusion of  $^{105}\text{Ag}$  and  $^{110\text{m}}\text{Ag}$  in lead single crystals at the two indicated temperatures.

not used in the evaluations of diffusivity and the effect  $E$ . Nonlinear weighted least-squares methods<sup>30</sup> were used to determine the coefficients of diffusion from the profiles of concentration in accordance with Eq. (5).

### C. Determination of Effect of Isotopic Mass

The relative ratio of isotopic concentrations can be expressed as

$$R(x_i) \propto \frac{C_\alpha(x_i)}{C_\beta(x_i)} \propto C_\alpha(x_i)^{-(D_\alpha/D_\beta - 1)}, \quad (6)$$

since the depth dependence of concentration of both isotopes is Gaussian within experimental error. Here  $\alpha$  and  $\beta$  are the two isotopes  $^{105}\text{Ag}$  and  $^{110\text{m}}\text{Ag}$ , respectively, and  $x_i$  is the mean distance of the  $i$ th slice from the sample surface. The values  $C_\alpha(x_i)$  were not directly measured, but are proportional to the values of total activity,  $C(x_i)$ , measured above for the profiles of concentration, within experimental error. We substituted the values  $C(x_i)$  for  $C_\alpha(x_i)$  because this substitution introduces negligible error. If the relative ratios  $R(x_i)$  can be determined experimentally, the exponent  $(D_\alpha/D_\beta - 1)$  can be derived from the data by fitting to Eq. (6). The effect of mass  $E$  is then easily calculated using Eq. (1).

The isotopic ratios  $R(x_i)$  must be measured with great precision in order to reliably determine the effect of isotopic mass. Such precision is necessary because the total variation of  $R(x_i)$  is always small; for these silver isotopes the maximum variation is 0.05 per order of magnitude of change in

$C(x_i)$ . Therefore, most investigators have measured  $R(x_i)$  to a precision of 0.1% over at least two orders of magnitude of change in  $C(x_i)$  to determine the effect of mass with an accuracy of about 10%. Such precise measurement has required that the sections be prepared and counted reproducibly with a statistical error of counting that is less than 0.1%; moreover, the dead time, background, and isotopic half-lives have been known with sufficient accuracy that negligible additional error has been introduced.

The possibility of systematic errors must also be critically examined. Such errors can result from radioactive impurities, variations in the self-absorption of the samples that are counted, and imperfect performance of the apparatus used for counting. Imperfect performance in counting can be caused by electronic drift, especially in the high-voltage supply, and other count-rate and energy-dependent effects. Such systematic errors must be minimized, and monitored during the course of an experiment to assure that gross errors do not contribute to the final result.

To avoid the systematic error that might arise from dependence on count rate, aliquots were taken from the vials of greater activity, thus reducing the span in count rate by an order of magnitude. Purity of the radioisotopes of silver was confirmed by  $\gamma$  spectroscopy. Systematic error caused by variation of the self-absorption of samples to be counted can be especially serious in this experiment because lead is a good absorber of  $\gamma$  radiation of low energy. Therefore, it is important that the same amount of lead be present in each bottle to be counted. To accomplish this, an appropriate amount of lead nitrate in solution was added to each of the bottles to be counted for the experiment performed at 300.0°C; in all other experiments, lead was removed from the original sectional solutions by precipitation as lead sulfate. Aliquots were taken from the vials of higher activity to reduce the span in count rate after removing the lead. The stability of the counter was monitored by counting both  $^{105}\text{Ag}$  and  $^{110\text{m}}\text{Ag}$  standard solutions frequently during the procedure for counting.

A critical test of the over-all validity of an experiment to determine the effect  $E$  is provided by simultaneously measuring the effect for an artificially prepared experiment having a null value of  $E$ . Such a measurement is an independent check of both the stability of the apparatus used for counting and the total experimental uncertainty in the values of  $R(x_i)$  and the effect  $E$ . We made such measurements by preparing, from a single vial derived from one section of each sample, solutions encompassing the entire experimental range of count rates, and counting them in the same manner and sequence as the sectional bot-

TABLE I. Measured values of the effect of isotopic mass on diffusivity of silver in pure lead and a Pb-Ag alloy.

Sample	$T$ ( $^{\circ}\text{C}$ )	Coefficient of diffusion $D_2$ ( $\text{cm}^2/\text{sec}$ )	Effect of isotopic mass $E$	"Null" value of effect $E$
Pb	300.0	$1.502 \times 10^{-7}$	$0.19 \pm 0.01$	$0.02 \pm 0.01$
Pb	303.1	$1.498 \times 10^{-7}$	$0.30 \pm 0.01$	$-0.01 \pm 0.03$
Pb	296.4	$1.258 \times 10^{-7}$	$0.25 \pm 0.01$	$0.00 \pm 0.01$
Pb	150.1	$1.589 \times 10^{-9}$	$0.31 \pm 0.02$	$0.00 \pm 0.01$
Pb + 0.08-at. % Ag	296.4	$1.236 \times 10^{-7}$	$0.26 \pm 0.02$	$0.00 \pm 0.01$

tles. Isotopic ratios and a value of  $E$  were calculated for each of these experiments in the same manner as for each sample. The resultant isotopic ratios should be constant within statistical error, regardless of the count rate, and the value of  $E$  that we obtain should therefore be null within experimental error.

Since the two isotopes  $^{105}\text{Ag}$  and  $^{110\text{m}}\text{Ag}$  are not completely separable by type of radiation or by energy discrimination, a method developed by Rothman *et al.*<sup>31</sup> was used to determine the isotopic ratios. The method consisted of counting the  $\gamma$  radiation simultaneously using the two discriminations in energy that are shown in Fig. 1 as  $L_1$  and  $L_2$ .  $L_1$  was set at a low energy to count most of the  $\gamma$  radiation from both isotopes, while  $L_2$  was set at an energy that best separates the  $^{105}\text{Ag}$  and  $^{110\text{m}}\text{Ag}$  spectra. Fine adjustment of these discriminators was made in such a way as to minimize errors that might arise from electronic drift in the counting apparatus. A multichannel analyzer was used to effect this adjustment. The dead times were determined by the two-source method. Bottles prepared for counting from sections of the samples, bottles prepared to measure a null value of  $E$ , and those containing isotopic standards were all counted using these discriminations in energy. After correction of these data for dead time and background, the relative isotopic ratios  $R(x_i)$  were calculated and corrected for radioactive decay.<sup>31-33</sup>

Calculation of the isotopic ratios involves the algebraic manipulation of several data,<sup>31</sup> each of which has a statistical uncertainty that arises from the statistics of counting. The statistical uncertainty of the ratios is hence larger than the statistics of counting for any of the raw data. A total of  $4 \times 10^6$  counts was collected for most of the data; the estimated standard deviations of the ratios due to the statistics of counting alone are approximately 0.1%.

### III. RESULTS

The coefficients of diffusion obtained by analysis of the profiles of concentration for the five experi-

ments are listed in Table I. All agree well with the results of Dyson *et al.*<sup>10</sup> The results for the effect of isotopic mass are presented in Fig. 3 as plots of  $\ln R(x_i)$  versus  $\ln C(x_i)$ . According to Eq. (6) such a plot should yield a straight line having the slope  $-(D_\alpha/D_\beta - 1)$ . A nonlinear weighted least-squares fit<sup>28</sup> to Eq. (6) was made to determine the value of the exponent  $(D_\alpha/D_\beta - 1)$  for each experiment; these values were then used to calculate the values of the effect  $E$  from Eq. (1). These values of  $E$  and the corresponding measurements of a null value of  $E$  are given in Table I. All quoted errors, including the error bars shown in Fig. 3, are the estimated standard deviations resulting from the statistical treatments.<sup>30</sup> These treatments have taken into account all experimental errors of any significance that can be calculated or estimated.

The three independent measurements of  $E$  for silver in pure lead close to  $300^{\circ}\text{C}$  demonstrate the reproducibility of our measurements. The similar value of  $E$  measured at  $150^{\circ}\text{C}$  indicates that the effect is not dependent on temperature; statistical tests confirm this. It is hence statistically proper to take a weighted average of the three results obtained close to  $300^{\circ}\text{C}$ . The resultant value of  $E$  is  $0.25 \pm 0.05$ . That the estimated

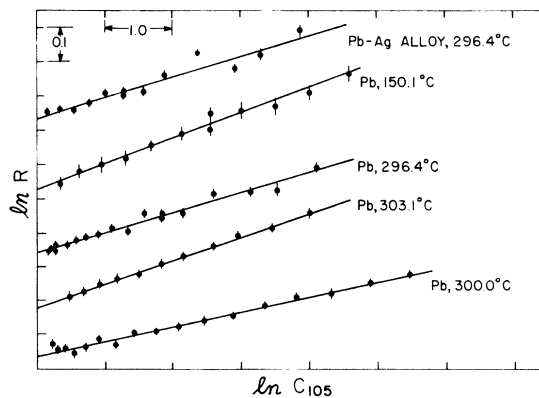


FIG. 3. Results of the five experiments to determine the effect of isotopic mass on diffusion of silver in single crystals of pure lead. The values of  $\ln C_{105}$  decrease from left to right.

standard deviations of 0.05 resulting from this statistical treatment is larger than those resulting from the error analyses of the individual experiments suggests that there are some additional errors. Nonetheless, this error of 0.05 is small enough to indicate that no unknown sources of serious error are present. The error is approximately the same as the total uncertainty of any of our previous measurements.<sup>34,35</sup>

The measured values of the effect are much smaller than the value of unity anticipated for a simple interstitial mechanism. Because the effect is unexpectedly small, systematic errors were investigated with great care. No systematic error of any consequence was found. The smallness of the estimated error ( $\pm 0.05$ ) for the effect and the reproducibility of the result in five independent determinations assures us that the effect is indeed very small compared with unity.

The measured effect is much smaller than other values recently reported.<sup>36</sup> This conflicting report does not indicate any errors serious enough to account for the great difference; nevertheless, certain experimental conditions of the other investigation may be unsatisfactory. For example, it appears that only one sample was used in the determination, and the effect was studied over only one order of magnitude in specific activity. Both of these conditions are especially risky when the profile of concentration shows a systematic departure from Gaussian behavior. Non-Gaussian behavior near the surface may result in an apparent increase in the value of  $E$ .<sup>37</sup> No attempt was made to measure a null value of  $E$  concurrently; moreover, it is doubtful that the counting of a standard solution of  $^{60}\text{Co}$ , which emits only  $\gamma$  rays of high energy, was an adequate check of electronic drift or stability with respect to the counting of  $^{105}\text{Ag}$ , which emits primarily  $\gamma$  rays of low energy. Furthermore, only  $10^5$  counts were collected from each section for separation of the isotopes by half-lives, and even fewer counts for the separation of  $\beta$  and  $\gamma$  radiation. The estimated error of the measured values of  $R(x_i)$ , due to the statistics of counting alone, was therefore much greater than the desired precision of 0.1%. Our experience<sup>38</sup> suggests that, under such conditions, it is difficult to measure a reliable value of the effect  $E$ . Consequently, we assert that the values of the effect of isotopic mass on diffusion of silver in lead are as reported herein, e. g.,  $0.25 \pm 0.05$  close to  $300^\circ\text{C}$ .

#### IV. DISCUSSION

##### A. Significance of Solute and Self-Diffusivities

The diffusivity  $D_2^0$  of silver in pure lead is extremely large<sup>10,39</sup> compared with the self-diffusi-

vity  $D_1^0$  of lead.<sup>28,40</sup> This and the apparently negligible effect of silver as solute on the self-diffusivity<sup>39</sup> led earlier investigators to propose that silver diffuses by the simple interstitial mechanism.<sup>10,39,41</sup> A more recent study has shown that a small linear enhancement of the self-diffusivity is caused by small additions of silver.<sup>9</sup> The observed enhancement is sufficiently small that the large diffusivity of silver can only be explained by a mechanism that involves the migration of interstitial defects.<sup>9</sup> Let us now consider the significance of the evidence in greater detail.

Enhancement of self-diffusivity in crystalline solids can arise because most mechanisms for diffusion of impurities are directly coupled to the self-diffusion. This direct diffusional coupling arises because atoms of solvent must jump to allow migration of an impurity. The atomic jumps of solvent and solute atoms may occur simultaneously, as for the direct interchange and ring mechanisms, or quite separately, as in the case of diffusion by vacancies<sup>15</sup> or interstitial-vacancy pairs.<sup>42</sup> The resultant linear enhancement of the self-diffusivity is characterized by an enhancement factor  $b$  according to the relation<sup>43</sup>

$$D_1 = D_1^0 (1 + bX_2) \quad (7)$$

Here  $D_1$  is the self-diffusivity in an alloy containing atomic fraction  $X_2$  of solute.

Theories<sup>15,42,44</sup> have satisfactorily interrelated the kinetics of solute and self-diffusion for the cases of solute diffusing by a simple vacancy, direct interchange, or bound interstitial-vacancy pair mechanism. These results indicate that the linear enhancement factor

$$b \geq f_0 (D_2^0 / D_1^0) \quad (8)$$

if the mechanisms for solute and self-diffusion are directly coupled. Here  $f_0$  is the correlation factor for self-diffusion in pure solvent. In Table II the measured value of  $b$  for additions of silver to lead is compared with the large values expected if silver migrated by one of these diffusional coupled mechanisms. It is evident that the large diffusivity of silver cannot be explained by a diffusional coupled mechanism.

The simple interstitial mechanism is usually considered unique in that migration of solute does not necessitate concomitant migration of solvent. We propose that this condition alone defines a more general interstitial mechanism for which other details of the process are not specified. Using this definition, we infer that approximately 80% or more of the solute diffusion occurs by an interstitial mechanism at  $300^\circ\text{C}$ . We must then seek a separate explanation for the finite value of  $b$ .

Although we have discussed the enhancement of diffusivity as arising only from diffusional cou-

TABLE II. Comparison of the experimental values of  $b$  and  $E$  obtained at 300 °C with the values expected for several diffusion mechanisms.

Parameters	Experimental results	Simple interstitial mechanism	Simple vacancy mechanism	Direct interchange mechanism	Bound interstitial-vacancy pair	Distortion interstitial mechanism <sup>a</sup>	Split interstitial mechanism <sup>a</sup>
$D_2^0/D_1^0$	875.0	...	...	...	...	...	...
$b$	136.8	0	>1675.3	680.4	680.4	0	0
$f_c$	...	1	~0	1	~0	1	1
$\Delta K$	...	1	~1	~1	~1	?	~1
$f_n$	...	1	1	0.34	1	1	0.20-0.34
$E$	0.25	1	~0	~0.34	~0	?	~0.20-0.34

<sup>a</sup>These mechanisms are described in the text.

pling, we must consider an alternate explanation. It has been proposed that the dissolution of solute might change macroscopic properties of the pure crystal and thereby change the activation energies of diffusive jumps.<sup>45</sup> If this latter effect were responsible for the observed increase in lead self-diffusivity, a comparable effect would be observed for diffusion of silver. A recent study of the diffusivity of silver in silver-doped lead alloys<sup>46</sup> shows that there is no similar effect on the silver diffusivity. Our present results are consistent with this result since the diffusivities in pure lead and the alloy containing 0.08-at.% silver at 296.4 °C are the same within experimental error (Table I). Therefore, we propose that a fraction of silver diffuses by a second, directly coupled mechanism; this second mechanism causes enhancement of the self-diffusivity of lead, but contributes only 20% or less to the solute diffusivity at 300 °C.

This second mechanism is probably not a direct interchange or ring type of mechanism because these processes are likely to have high activation energies.<sup>47</sup> It is more reasonable to presume that vacancies, which are generally responsible for self-diffusion in face-centered cubic metals,<sup>19</sup> associate with an interstitial or substitutional solute, causing the increase in self-diffusivity. The high value of  $b$  indicates that the solute binds strongly to vacancies. Theory<sup>48</sup> and experiment<sup>35,40</sup> suggest that the electrostatic interaction of a substitutional impurity with a vacancy is well screened in lead, and thus small. It is therefore expected that substitutional solute atoms would bind only weakly to vacancies, diffuse at about the same rate as solvent atoms, and produce little enhancement. Alternatively, it is more plausible that interstitial solute atoms bind attractively to vacancies.<sup>9,35,42</sup> These interstitial-vacancy pairs may diffuse in a manner similar to that proposed,<sup>42</sup> and produce the observed enhancement of lead self-diffusivity.<sup>9</sup>

#### B. Significance of Small Effect of Isotopic Mass

Assuming that silver does diffuse by two mech-

anisms, the total diffusivity  $D$  may be expressed as the sum of the two respective contributions  $d^{(1)}$  and  $d^{(2)}$ , i. e.,  $D = d^{(1)} + d^{(2)}$ . Using Eq. (1), we may then write the observed effect  $E$  in terms of the effects  $e^{(1)}$  and  $e^{(2)}$  for the separate mechanisms,

$$E = \frac{d^{(1)}}{D} e^{(1)} + \frac{d^{(2)}}{D} e^{(2)} . \quad (9)$$

The interstitial-vacancy pair mechanism, believed to be the second, coupled mechanism, has by its very nature a very strong correlativity. The factor  $f_c$  and the effect of mass  $e^{(2)}$  of this mechanism are then small and dependent on temperature. Since the factor  $d^{(2)}/D$  of Eq. (9) is also small, we expect that the contribution of this mechanism to the total effect  $E$  is of the order of the experimental error, i. e., 20%. Since we detect no dependence of  $E$  on temperature, we propose that the measured values of  $E$  are essentially those for the predominant mechanism.

If the predominant mechanism is an interstitial one, the effect of mass is expected to be independent of temperature. As is shown in Table I, this expectation is realized over a great range in the diffusivity, within experimental error. It is likely that the three factors  $f_c$ ,  $\Delta K$ , and  $f_n$  are also independent of temperature for the predominant mechanism, and that one of these factors is small. We therefore propose that the predominant mechanism for silver diffusion in lead is interstitial, but is strongly perturbed by one of the three coupling mechanisms discussed in Sec. I.

The factor  $f_c$  for diffusion of a solute by an interstitial mechanism can be small if two or more interstitial solute atoms are tightly bound and diffuse with little dissociation. We suggest that the major contribution to the diffusivity must be from clusters of three or more interstitial solute atoms to yield a value of  $f_c$  as low as the observed value of  $E$ . Since we observe no temperature dependence of  $E$ , these clusters must be so tightly bound

that virtually no dissociation occurs. The preferred interstitial site and configurations of such clusters must also be consistent with the observed internal-friction effects.<sup>4</sup> Although this explanation of the low value of  $E$  is quite possible, we prefer to seek an explanation that involves defects of lesser complexity.

Let us now assume that the predominant mechanism involves single solute atoms diffusing by an interstitial mechanism; we expect that  $f_c = 1$  in this case. Although most evidence suggests that  $\Delta K$  is close to unity,<sup>17,19-23</sup> it is possible<sup>49</sup> that distortion of the lattice around a metallic interstitial such as silver might be very large and participate strongly in the process of jumping. In such a case, most of the activation energy for diffusion might be required to move the distortion. The kinetic factor could then be small. Such large distortions should also be sufficient to cause a change of the activation energy<sup>45</sup> for solute diffusion with additions of solute. The absence of an observable effect<sup>46</sup> suggests that the associated distortions are also too small to cause a significant reduction in  $\Delta K$ .

Rossolimo and Turnbull<sup>3</sup> and Turner *et al.*<sup>4</sup> suggest that split interstitials may be the predominant solute defect for the similar case of gold dissolved in lead. A split interstitial consists of two atoms sharing a lattice site in such a way that neither is located at the site. This defect can give rise to the observed internal-friction effects.<sup>4</sup> If the split interstitial consists of two silver atoms, the process of migration should produce an enhancement of the self-diffusion that is several times larger than the observed effect.<sup>9</sup> We therefore propose that interstitial silver atoms do not associate significantly with each other.

A split interstitial consisting of a solute and a solvent atom, however, may migrate without causing a concomitant enhancement of the self-diffusion. This defect may make rotational jumps between equivalent orientations, and dissociative jumps. The defect may dissociate by the jump of a solute atom from association with one lead atom to association with a neighboring lead atom, thus sharing a new site. This jump requires the adjustment of position of both the original and the neighboring lead atoms. Both jumps cause no enhancement of the self-diffusivity, but reduce the effect of mass through the factor  $f_n$  of Eq. (4). For the rotational jumps,  $n = 2$  and  $f_n = 0.34$ ; for dissociative jumps,  $n = 3$  and  $f_n = 0.20$ . The application of Eq. (4) to such a complex process is naive, but there exists

no theory for  $f_n$  or  $\Delta K$  which would permit a more rigorous treatment for this case. We thus accept the above values as a best estimate of this coupling effect. Assuming that  $f_c = 1$  and  $\Delta K = 1$ , the effect of isotopic mass for this mechanism should lie between 0.20 and 0.34. The agreement with our experimental results is surprisingly good.

## V. CONCLUSION

Experimental evidence indicates that silver diffuses in lead by two mechanisms. One, most probably the interstitial-vacancy pair mechanism, causes the enhancement of lead self-diffusivity with silver additions, but contributes only about 20% to the total silver diffusivity and probably a lesser amount to the measured effect of isotopic mass. The predominant mechanism for the diffusion of silver is an interstitial mechanism which manifests a small temperature-independent effect of mass. Although we are unable to specify this mechanism in detail, the small value of the effect  $E$  indicates that migration of the solute defect is strongly coupled to the solvent lattice. We suggest that the solute defect might be either a split interstitial consisting of a solute and solvent atom, or a single interstitial solute atom surrounded by a large distortion of the lattice. Finally, it is noteworthy that the solute silver couples strongly to the solvent lattice in two reciprocal ways; it acts on the lattice to cause enhancement of the self-diffusivity, and is acted upon by the lattice to decrease the effect of isotopic mass.

Interstitial defects and their migration can be quite complex. More experimental work on a variety of interstitial solid solutions will eventually lead to a better specification of the types of interstitial defects, the energetics of their formations and the kinetics of their migration.

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