# Diffusion of Sb<sup>124</sup>, Cd<sup>109</sup>, Sn<sup>113</sup>, and Zn<sup>65</sup> in tin\*†

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The anisotropic diffusion coefficients of Sb<sup>124</sup>, Cd<sup>109</sup>, and Zn<sup>55</sup> in single crystals of tin have been measured by the tracer-sectioning method. The results of the measurements are for Sb,  $D_{\parallel} = 71 \exp[-(29.0 \pm 0.03 \text{ kcal/mol})/R T]$ ,  $D_{\perp} = 73 \exp[-(29.4 \pm 0.4 \text{ kcal/mol})/R T]$ ; for Cd,  $D_{\parallel} = 220 \exp[-(28.2 \pm 0.6 \text{ kcal/mol})/R T]$ ,  $D_{\perp} = 120 \exp[-(27.6 \pm 0.5 \text{ kcal/mol})/R T]$ ; for Zn,  $D_{\parallel} = 1.1 \exp[-(12.0 \pm 0.4 \text{ kcal/mol})/R T]$ ,  $D_{\perp} = 8.4 \exp[-(21.3 \pm 0.2 \text{ kcal/mol})/R T]$ , all in cm<sup>2</sup>/sec. The literature values for self-diffusion in tin were also checked by a separate experiment. Considerable persistence was needed to find an effective electroplating procedure for zinc diffusion in tin. The low values of diffusivity of Sb and Cd strongly indicate a substitutional-vacancy mechanism. Divalent zinc has the same valence as cadmium but diffuses fairly fast, somewhat like the noble-metal solutes. In contrast with monovalent and most divalent solvents, there appears to be no systematic variation of activation energy for the impurity diffusion in tin are discussed. A revision in method for the calculation of the migration energy for impurity diffusion is indicated.

#### INTRODUCTION

The diffusivities of Sn,<sup>1-3</sup> In,<sup>4</sup> Au,<sup>5</sup> and Cu<sup>6</sup> in single-crystal tin have been measured in recent years. Originally the vacancy mechanism was thought to be responsible for self-diffusion in tin<sup>2</sup> and this has been supported by high-pressure experiments<sup>3</sup> measuring the activation volume. However, in contrast with self-diffusion, the noble metals have very large diffusivities in tin, an order of magnitude greater than that for self-diffusion. Moreover, they exhibit very striking anisotropy favoring motion along the c axis. From an examination of the crystal structure of white tin, Dyson<sup>°</sup> was led to suggest that these noble-metal solutes are migrating by an interstitial mechanism. In a similar guadrivalent metal, lead, noblemetal impurities also diffuse rapidly. Since the ratio of noble-metal atomic diameter and lead atomic diameter is in the range of 0.7-0.8, interstitial solid solution would not be supposed<sup>7</sup> to form in this system; Dyson et al.<sup>8</sup> concluded that it is ionic radius rather than atomic radius which determines the possibility of forming an interstitial solid solution. To understand why the noble metal has the interstitial character in polyvalent lead or tin, Anthony and Turnbull<sup>9</sup> proposed the d-d correlation binding between the ion cores. They pointed out this binding is present only when the noble metal is at the interstitial rather than the substitutional site in Pb, Sn, Tl, In, and Cd. Interestingly enough, reports on zinc diffusion in polycrystal tin<sup>10</sup> show a large diffusivity similar to the noble-metal solutes. On the other hand, the noble-metal solutes diffuse in Cd<sup>11</sup> by vacancy mechanism contrary to the prediction made by Anthony and Turnbull. There is speculation that

a strongly oscillating potential, rather than a monotonic potential, might cause quite a different behavior in a polyvalent solvent rather than in a monovalent one. Cd, Sb, and Zn were chosen as solutes in this study to explore the valence effect on impurity diffusion in a polyvalent metal.

### **EXPERIMENTAL PROCEDURES**

Single crystals of tin were grown by the Bridgman method from 99.999% pure tin, obtained from Cominco. Acceptable single crystals  $\frac{1}{2}$  in. in diameter were cut by an acid string saw into  $\frac{3}{8}$ -in. long specimens. Most single crystals showed a specimen orientation perpendicular to the *c* axis. To obtain the orientation parallel to the *c* axis, specimens were machined transversely out of the single-crystal cylinders.

All radio isotopes  $Sn^{113}$ ,  $Cd^{109}$ ,  $Sb^{124}$ , and  $Zn^{65}$ were supplied by New England Nuclear Corp. in a hydrochloric acid solution. A great deal of effort was required to electroplate zinc. Most of the early runs gave erratic, non-Gaussian-penetration profiles. To overcome these difficulties. various types of plating baths were tried. The cyanide bath, even though it gave good results for electroplating Cd and Sn, was found to be unsatisfactory for plating zinc. After dozens of trials, we were able to get one Gaussian-penetration profile by using slightly acid zinc bath. In the process of plating in the acid bath, oxygen was liberated and acid was formed. As zinc was plated out and acid accumulated, the cathode efficiency was lowered. To avoid the accumulation of acid, the acidity of the bath was maintained approximately constant (in the range of pH = 6-8) by adding appropriate amounts of NH<sub>4</sub>OH or NAOH solution.

Unfortunately, results were still irreproducible.

9

TABLE I. Arrhenius constants for self-diffusion and impurity diffusion in tin.

Isotope	Diffusion direction	$A$ $(cm^2/sec)$	Q (kcal/mole)
Sb <sup>124</sup>		71.0 + 22.0 - 17.0	$29.0 \pm 0.3$
$\mathrm{Sb}^{124}$	Ţ	73.0 + 36.0 - 24.0	$29.4 \pm 0.4$
Sn <sup>113</sup>	II	12.8 + 5.9 - 4.1	$26.0 \pm 0.4$
Sn <sup>113</sup>	T	21.0 + 6.4 - 4.9	$25.9 \pm 0.5$
Cd <sup>109</sup>	11	$220.0 \begin{array}{c} +182.0 \\ -99.0 \end{array}$	$28.2\pm0.6$
Cd <sup>109</sup>	T	120.0 + 89.0 - 51.0	$27.6 \pm 0.5$
$\mathbf{Zn}^{65}$	11	$\begin{pmatrix} 1.1 + 0.5 \\ - 0.4 \end{pmatrix} \times 10^{-2}$	$12.0\pm0.4$
$Zn^{65}$	T	8.4 + 2.6 - 2.0	$21.3 \pm 0.2$

Neither raising the temperature of the bath during plating nor using a fresh batch of isotope for each specimen nor careful etching of the sample prior to plating seemed to be the answer. After further experimentation the following successful procedure was finally developed and was used in all the zinc-diffusion experiments reported here. The specimen was etched in alcohol with 2% HCl, electroplated in the Zn<sup>65</sup> plating bath for 3 min, removed from this bath and dipped into a solution made up of 5-g/liter SnCl<sub>2</sub>· 2H<sub>2</sub>O, 5. 6-g/liter NaOH, and 50-g/liter NaCN for 1 min. Next it was returned to the plating bath where the pH was, as before, maintained constant. Thirty minutes electroplating was enough. The specimen was then removed from the zinc bath, quickly rinsed in alcohol and then in acetone, and blotted dry.

Two samples, perpendicular and parallel to the c axis, were placed face to face and separated by a Pyrex disk to minimize the evaporation of the tracer material. They were sealed under vacuum in Pyrex capsules. The diffusion anneals were carried out in nichrome-wound furnaces, and lasted from 5 to 20 days for Cd diffusion, from 6 days to 3 months for Sb diffusion, and from 2 h to 4 days for Zn diffusion. The temperatures were maintained within  $\pm 0.3$  °C.

After the diffusion anneals, the diffusion coefficients were obtained by the standard lathe-sectioning and radioactive-counting techniques.

### RESULTS

A good linear plot of the logarithm of the specific activity versus the square of the penetration depth was obtained in all successful runs; a typical curve for Zn diffusion is shown in Fig. 1. The frequency factors and the activation energies for the parallel and perpendicular diffusion, as obtained from a least-squares analysis, are listed in Table I. The logarithms of the diffusion constants are plotted as a function of the reciprocal temperature in Figs. 2-5 for Sn<sup>113</sup>, CD<sup>109</sup>, Sb<sup>124</sup>, and Zn<sup>65</sup>, respectively.

For any quantitative interpretation of these data some account must be taken of the influence of the correlation factor. The next section develops a treatment for evaluating this quantity for the tin lattice.

# CORRELATION FACTOR FOR VACANCY DIFFUSION IN TIN

It is well known that for a cubic crystal the correlation factor can be simplified to a function of  $\langle \cos \theta \rangle$ , the average cosine of the angle between successive atom jumps. A considerable number of papers<sup>12-16</sup> dealing with  $\langle \cos \theta \rangle$  by different methods have been published. Howard<sup>17</sup> has extended the expression for correlation factor to cover general cases including unequivalent jumps condition.

For all jumps equivalent, the correlation factor



FIG. 1. Sample penetration plots for  $Zn^{65}$ . Note that the abscissas of the graphs are to be multiplied by factors in the upper-right-hand corner of figure.

DIFFUSION OF Sb<sup>124</sup>, Cd<sup>109</sup>, Sn<sup>113</sup>, AND Zn<sup>65</sup> IN TIN



FIG. 2. Diffusion coefficients vs 1/T for tin self-diffusion.

can be calculated as a numerical constant; however, for impurity diffusion  $\langle \cos \theta \rangle$  depends on the ratio of the impurity jump frequency to that of the neighboring solvent atoms; therefore, the correlation factor for impurity diffusion is dependent on the ratio of jump frequencies.

Since white tin has a tetragonal structure, it is more convenient to calculate the partial correlation factor. The expression for the *j*th component of the *i*th-type jump correlation factor can be written  $as^{18}$ 

$$f_{i,j} = 1 + 2\sum_{n=1}^{\infty} \frac{\overline{\lambda}_{i,j} \cdot \overline{\lambda}_{n(i)}}{(\lambda_{ij})^2} , \qquad (1)$$

where  $\lambda_{i,j}$  is the *j*th component of the *i*th jump for the diffusing atom and  $\lambda_{n(i)}$  is the *n*th jump of the diffusing atom that followed the *i*th type in question. We introduce the vector<sup>19</sup>

$$\vec{\mathbf{S}}_{i} = \sum_{n=1}^{\infty} \vec{\lambda}_{n(i)} , \qquad (2)$$

which can be thought of as a "history vector" that gives the average final displacement of the tracer in any configuration. If the jump frequencies are known, one can solve for the  $S_i$  by a recursion relation as follows:

$$\vec{\mathbf{S}}_{i} = \frac{\sum_{m} \omega_{m} \vec{\mathbf{S}}_{m} - \omega_{r} \vec{\lambda}_{i}}{\sum_{m} \omega_{m}} , \qquad (3)$$

where  $\omega_m$  represents the set of jump frequencies available to the vacancy after the *i*th jump and  $\omega_r$ the reverse impurity-vacancy jump. From Eqs. (1) and (2) we have

$$f_{i,j} = 1 + 2 \,\overline{\mathbf{S}}_i \cdot \overline{\mathbf{j}} / (\overline{\lambda}_{i,j}), \qquad (4)$$

where j is the unit vector in the *j*th direction.

Let the z axis be parallel to the c axis of the white tin. For a nearest-neighbor-vacancy site B adjoining the diffusing atom and a next-nearestneighbor-vacancy site A adjoining the impurity. the following respective frequencies are pertinent (see Fig. 6):  $\omega_{\rm B}$ , exchange of diffusing atom with the vacancy at site B;  $\omega_a$ , jump of B to P site adjoining to A site;  $\omega_c$ , jump of B to a more distant site;  $\omega_{a'}$ , jump of A to the nearest-neighboring site which adjoins B site;  $\omega_A$ , exchange of diffusing atom with the vacancy at site A;  $\omega_{c'}$ , jump of A to a more distant site which does not adjoin the diffusing atom. For the jumps of the vacancy starting at P there are  $\omega_p$ , jump of P to B site;  $\omega_{p'}$ , jump of P to A site, and  $\omega_{d}$ , jump of P to a more distant site. The  $\lambda_A$  and  $\lambda_B$  are jump lengths for the diffusing atom. All vectors  $\mathbf{\tilde{S}}_i$  can be ex-



FIG. 3. Diffusion coefficients vs 1/T. Cd<sup>109</sup> diffusion in tin.



FIG. 4. Diffusion coefficients vs 1/T. Sb<sup>124</sup> diffusion in tin.

pressed in terms of components parallel and perpendicular to the c axis of the tetragonal axis. For simplicity, we shall assume that, to take into account the effective dissociation rate, all frequencies of vacancies jumping away to a non-nearestneighbor site are to be multiplied by a constant fraction F. F is defined as the fraction of dissociating vacancies (those from the jumps which move a vacancy away from a diffusing atom) that do not recombine with the impurity. The assumption of a constant F might cause errors in the f's of a few percent. Using Eq. (3) we have the appropriate recursion relation for  $\vec{S}_i$ :

$$(\omega_{B} + 2F\omega_{a} + 3F\omega_{c})S_{\parallel B} = 2F\omega_{a}S_{\parallel p} + F\omega_{c}\sum^{A}S_{\parallel c} - \omega_{B}(\lambda_{\parallel B} + S_{\parallel B}),$$

$$(\omega_{A} + 4F\omega_{a'} + F\omega_{c'})S_{\parallel A} = 4F\omega_{a'}S_{\parallel p} + F\omega_{c'}S_{\parallel c'} - \omega_{A}(\lambda_{\parallel A} + S_{\parallel A}),$$

$$(6)$$

$$(\omega_{p} + \omega_{p'} + 4F\omega_{d})S_{\parallel p} = \omega_{p}S_{\parallel B} + \omega_{p'}S_{\parallel A} + F\omega_{d}\sum^{4}S_{\parallel d}, \qquad (7)$$

$$(\omega_{B} + 2F\omega_{a} + 3F\omega_{c})S_{\perp B} = 2F\omega_{A}S_{\perp p}$$

$$+F\omega_{c}\sum^{3}S_{\perp c} - \omega_{B}(\lambda_{\perp B} + S_{\perp B}),$$
(8)
$$(\omega_{p} + \omega_{p'} + 4F\omega_{d})S_{\perp p} = \omega_{p}S_{\perp B} + \omega_{p'}S_{\perp A} + F\omega_{d}\sum^{4}S_{\perp d}.$$
(9)

Neglecting the more distant position on the basis that S falls off rapidly with distance we then have

$$S_{\parallel B} = \frac{2F\omega_a S_{\parallel p} - \omega_B \lambda_{\parallel B}}{2\omega_B + 2F\omega_a + 3F\omega_c} , \qquad (10)$$

$$S_{\parallel A} = \frac{4F\omega_a, S_{\parallel p} - \omega_a \lambda_{\parallel A}}{\omega_A + \omega_B + 4F\omega_a + F\omega_{c'}}, \qquad (11)$$

$$S_{\parallel p} = \frac{\omega_p S_{\parallel \underline{B}} + \omega_{p'} S_{\parallel \underline{A}}}{\omega_p + \omega_{p'} + 4 F \omega_d} , \qquad (12)$$

$$S_{\perp B} = \frac{2F\omega_a S_{\perp D} - \omega_B \lambda_{\perp B}}{2\omega_B + 2F\omega_a + 3F\omega_c} , \qquad (13)$$

$$S_{\perp p} = \frac{\omega_p S_{\perp B}}{\omega_p + \omega_{p'} + 4F \,\omega_d} \,. \tag{14}$$

From Eqs. (13) and (14) we have

$$S_{\perp B} = \frac{2F\omega_a\omega_p S_{\perp B} - \omega_B(\lambda_{\perp B} + S_{\perp B})(\omega_p + \omega_{p'} + 4F\omega_d)}{(\omega_B + 2F\omega_a + 3F\omega_c)(\omega_p + \omega_{p'} + 4F\omega_d)} .$$
(15)

The x component of B-type-jump correlation factor is obtained by substituting Eq. (15) into Eq. (4),



FIG. 5. Diffusion coefficients vs 1/T. Zn<sup>65</sup> diffusion in tin.

DIFFUSION OF 
$$Sb^{124}$$
,  $Cd^{109}$ ,  $Sn^{113}$ , AND  $Zn^{65}$  IN TIN 1483

$$f_{B,x} = \frac{2F\omega_a(\omega_{p'} + 4F\omega_d) + 3F\omega_c(\omega_p + \omega_{p'} + 4F\omega_d)}{2F\omega_a(\omega_{p'} + 4F\omega_d) + 3F\omega_c(\omega_p + \omega_{p'} + 4F\omega_d) + 2\omega_B(\omega_p + \omega_{p'} + 4F\omega_d)}$$
(16)

Substituting Eq. (12) into Eq. (10) and Eq. (11) to eliminate  $S_{\parallel p}$ , we have the simultaneous equations for  $S_{\parallel p}$  and  $S_{\parallel A}$ :

$$S_{\parallel B}\left(2\omega_{B}+2F\omega_{a}+3F\omega_{c}-\frac{2F\omega_{a}\omega_{p}}{\omega_{p}+\omega_{p'}+4F\omega_{d}}\right)=\frac{2F\omega_{a}\omega_{p'}}{\omega_{p}+\omega_{p'}+4F\omega_{d}}S_{\parallel A}-\lambda_{\parallel B}\omega_{B},$$
(17)

$$S_{\parallel A}\left(2\omega_{A}+4F\omega_{a}+F\omega_{c}-\frac{4F\omega_{a}\omega_{p}}{\omega_{p}+\omega_{p'}+4F\omega_{d}}\right)=\frac{4F\omega_{p}\omega_{a}}{\omega_{p}+\omega_{p'}+4F\omega_{d}}S_{\parallel B}-\lambda_{\parallel A}\omega_{A}.$$
(18)

Using  $\lambda_{\parallel A} = c$ ,  $\lambda_{\parallel B} = \frac{1}{4}c$  and  $f_A = 1 + 2S_{\parallel A}/\lambda_{\parallel A}$ ,  $f_{B,z} = 1 + 2S_{\parallel B}/\lambda_{\parallel B}$ , we get

$$\frac{1}{8} \left( 2\omega_B + 2F\omega_a + 3F\omega_c - \frac{2F\omega_a\omega_p}{\omega_p + \omega_{p'} + 4F\omega_d} \right) f_{B,z} - \frac{F\omega_a\omega_{p'}}{\omega_p + \omega_{p'} + 4F\omega_d} f_{A,z} = \frac{1}{4}F\omega_a + \frac{3}{8}F\omega_c - \frac{F\omega_a(\omega_p + 4\omega_{p'})}{4(\omega_p + \omega_{p'} + 4F\omega_d)} , \qquad (19)$$

$$\frac{F\omega_{p}\omega_{a'}}{2(\omega_{p}+\omega_{p'}+4F\omega_{d})}f_{B,z} - \frac{1}{2}\left(2\omega_{A}+4F\omega_{a'}+F\omega_{c}-\frac{4F\omega_{a'}\omega_{p'}}{\omega_{p}+\omega_{p'}+4F\omega_{d}}\right)f_{A,z} = -2F\omega_{a'}-\frac{1}{2}F\omega_{c'}+\frac{F\omega_{a'}(\omega_{p}+4\omega_{p'})}{2(\omega_{p}+\omega_{p'}+4F\omega_{d})}.$$

$$(20)$$

Then the correlation factors parallel to the c axis can be evaluated. In the next paragraph we show how to estimate F by comparison with Mullen's calculation<sup>18</sup> for the primitive tetragonal lattice.

Each atom in white tin has four nearest neighbors and two next nearest neighbors; it follows that



FIG. 6. Configurations for the vacancy mechanism in body-centered tetragonal tin.

$$\frac{D_{\parallel}}{D_{\perp}} = \frac{1}{2} \left(\frac{c}{a}\right)^2 \left(\frac{8\omega_A f_{A,\varepsilon}}{\omega_B f_{B,x}} + \frac{f_{B,\varepsilon}}{f_{B,x}}\right) .$$
(21)

Using the values of f from Mullen's<sup>18</sup> calculation for the primitive tetragonal lattice, we were able to calculate the values of  $(D_{\rm II}/D_{\rm I})(a/c)^2$  from this equation, as a function of  $\omega_A/\omega_B$ , the ratio of frequencies for jumps to A site and B site. We then determined  $\omega_A/\omega_B$  by comparison with the experimental values for  $(D_{\rm II}/D_{\rm I})(a/c)^2$  over the range of temperature available. In our experiments, the following equation is obtained by fitting to the selfdiffusion data:

$$\omega_{A0}/\omega_{B0} = 0.26 \exp[-(0.315 \text{ kcal/mole})/RT].$$
 (22)

For RT = 0.95 kcal/mole, or at temperature 205.1 °C,  $\omega_{A0}/\omega_{B0} = 0.189$ , which gives  $f_{B,x,0} = 0.543$ , the correlation factor for self-diffusion in tin along the *a* axis. In the case of self-diffusion, all jump frequencies in Eq. (16) are equal to either  $\omega_{A0}$  or  $\omega_{B0}$ . From the known value of  $f_{B,x,0}$ , F = 0.707 is estimated. The correlation correction for the *B*-jump activation energy of selfdiffusion can be evaluated by using Eq. (16) and Eq. (22). For RT = 0.95 kcal/mole,

$$C_{B0} = R \frac{\partial \ln f_{B,x,0}}{\partial (1/T)} = -0.015 \text{ kcal/mole}, \qquad (23)$$

TABLE II. Correlation factors and Y as a function of temperature for self-diffusion.

1000/ <i>T</i> (° K <sup>-1</sup> )	$\omega_{A0}/\omega_{B0}$	f <sub>B,x,0</sub>	f <sub>B,z,0</sub>	f <sub>A,0</sub>	$Y (cm^2/sec)$
2.00	0.192	0.544	0.537	0.893	4.17×10 <sup>-11</sup>
2.09	0.189	0.543	0.536	0.895	$1.26 \times 10^{-11}$
2.20	0.186	0.542	0.554	0.897	2.96×10 <sup>-12</sup>

5

( cm<sup>z</sup> / sec ) -- ō<sub>-</sub>



 $10^{32}$  1 1 1 1 2.00 2.05 2.10 2.15 2.20  $10^{3}$  / T (°K<sup>-1</sup>)

FIG. 7. A plot of Y vs 1/T to determine  $H_A^f + H_A^m$ .

which shows that the correlation factor for selfdiffusion in tin is almost independent of temperature.

### ENERGY CONSIDERATION FOR SELF-DIFFUSION IN THE PARALLEL DIRECTION

Both A jump and B jump contribute to the parallel diffusion in tin. Manipulating the expressions for  $D_{\parallel}$  and  $D_{\perp}$ , we have

$$D_{II} = \frac{1}{6} c^{2} \nu_{A} f_{A,z} e^{\Delta S_{A}/R}$$

$$\times e^{-(H_{A}^{f} \star H_{A}^{m})/RT} + \frac{1}{2} (c/a)^{2} \frac{f_{B,z}}{f_{B,x}} D_{1}$$
or

$$\left( D_{\parallel} - \frac{c^2}{2a^2} \frac{f_{B,z}}{f_{B,x}} D_{\perp} \right) / f_{A,z}$$
  
=  $\left( \frac{1}{6} c^2 \right) \nu_A e^{\Delta S_A / R} e^{-(H_A^f + H_A^m) / RT} .$  (24)

For tin,  $\frac{1}{2}(c/a)^2 = 0.149$ . We define

$$Y = Y_0 e^{-(H_A^f + H_A^m)/RT} , \qquad (25)$$

where

$$\begin{split} Y = & \left( D_{\parallel} - \ 0. \ 149 \ \frac{f_{B,z}}{f_{B,x}} \ D_{\perp} \right) \middle| f_{A,z} \quad , \\ & Y_0 = \left( \frac{1}{6} \, c^2 \right) \, \nu_A e^{\, \Delta S \, A^{/R}} \; . \end{split}$$

For self-diffusion, the values of  $f_{B,s,0}$  and  $f_{A,s,0}$  can be calculated from the two simultaneous equa-

tions (19) and (20). With three values of  $\omega_{A0}/\omega_{B0}$  calculated at three different temperatures 1000/T = 2.00, 2.09, and 2.20, the values of  $f_{B,z,0}, f_{A,z,0}$ , and Y are compiled in Table II. A plot of Y vs 1000/T on a semilog scale is shown in Fig. 7. These three points lie fairly well on a straight line; the slope of this straight line gives the value of  $H_A^f + H_A^m = 26.3 \pm 0.1$  kcal/mole, in good agreement with the experimental result,  $26.0 \pm 0.4$  kcal/mole. It follows that the C for parallel self-diffusion is also small.

### DISCUSSION

As indicated in Fig. 2, the c axis Arrhenius plot of the present work for self-diffusion essentially coincides with that by Meakin and Klokholm,<sup>2</sup> while the values of  $D_{\mu}$  by Coston and Nachtrieb<sup>3</sup> are lower. In general, the absolute values of D are in good agreement with the previous two studies, except for the region of low temperature along the *a* axis. The examination of the values of the preexponential factor and activation energy of this experiment lend support to the vacancy mechanism for selfdiffusion. Cd diffusion in tin shows a small anisotropy favoring motion in the plane perpendicular to the tetragonal axis. The diffusivities in both directions are larger than that of self-diffusion along the c axis, but smaller than that along the a axis. Both frequency factor and activation energy for Cd diffusion are larger than those for self-diffusion. The low values of diffusivity of Cd strongly indicate a substitutional vacancy mechanism.

The results of this work and that of the earlier research for other impurities diffusing in tin are shown graphically in Fig. 8. There are two quite clearly separated categories: one group of noblemetal solutes whose diffusivities and anisotropies are very large, the other of multivalent metal solutes with an order of magnitude smaller diffusivities and anisotropies. An exception is divalent zinc, which has the same valence as Cd, but diffuses fairly fast, somewhat like the noble-metal solutes. Perhaps, the difference in ion size between zinc (0.74 Å) and cadmium (0.97 Å) is crucial in causing this marked difference in behavior as impurity in tin.

The ionic charge of solute and solvent atoms is the only factor considered in the treatment of the electrostatic interaction theory.<sup>20,21</sup> According to this theory, there should be a systematic variation of activation energy with valence of the diffusing ion. The impurity atoms with larger valence than that of solvent atoms diffuse faster, since its positive Thomas-Fermi potential attracts more vacancies at neighboring sites.

The standard shielded ion model with a Thomas-Fermi-type potential has proved to give satis-



FIG. 8. Diffusion coefficients vs 1/T for impurity diffusion in tin.

factory predictions as to the qualitative behavior of  $H_m$  and  $H_f$  for both heterovalent and homovalent impurities in monovalent metals.<sup>20-23</sup> The same general behavior seems to hold qualitatively for the divalent solvents,  $zinc^{24-27}$  and cadmium, <sup>11</sup> although there is indication of effective oscillations in the potential from a study of impurity enhancement.<sup>28</sup> For impurities in magnesium<sup>29</sup> the results appear to be in almost direct contradiction to the expectations of the simple shielded ion model. On going to trivalent solvents there seems to be, in the case of aluminum, a very small valence dependence of the Q's for most solutes<sup>30, 31</sup> which come close to the Q for self-diffusion. However, the transition-metal impurities have values considerably higher. Recent work on impurities in tin<sup>32,33</sup> show a somewhat inverted picture.

Off hand, one might tend to attribute this change or apparent inversion of the effect of valence difference as due to the well-known Friedel oscillations<sup>34, 35</sup> which are pulled in to small r-values for the higher valence solvents.

For example, the antimony tracer has five valence electrons, but diffuses slower than the tin tracer with  $D_{\parallel} > D_{\perp}$ , in contrast to what has been

found as the influence of valence for monovalent and divalent solvents. Suppose the Sb diffusion in tin operates by the vacancy mechanism and the potential around the diffusing ion is of the oscillating type. In that case, the oscillating potential at the nearest-neighbor sites due to the antimony tracer (Z = +1) might be negative, and not positive as in the Thomas-Fermi approximation. Hence the vacancy is not attracted to the antimony and finds it more favorable to occupy a next-nearestneighbor site along the *c* axis rather than one of the four nearest-neighbor sites. This qualitative argument might help explain why the diffusion of antimony in the parallel direction is faster than that in the perpendicular direction.

Quantitative treatments of the variation of activation energy for diffusion with solute usually use as a starting point the equations

$$\Delta Q = \Delta H_f + \Delta H_m - \Delta C, \qquad (26)$$

where  $C \equiv R[d\ln f/d(1/T)]$  as in Eq. (23). As we indicate in the preceding paragraph, it is easy to see how the greater importance of the Friedel oscillation may affect  $\Delta H_f$ . The difficulty comes in evaluating the sum  $\Delta H_f + \Delta H_m$  where the dominant contribution is generally taken<sup>23,36</sup> to be the interaction of the moving atom with two semivacancies at the positions  $\frac{11}{16}$  times the interatomic distance on either side of the atom. In some  ${\tt cases}^{{\tt 29,30}}$  the oscillating potential model appears not to be a substantial improvement over the Thomas-Fermi approach. Remarkably good agreement<sup>37</sup> has evolved for oscillating potentials empirically fit to the transition-metal impurities in aluminum but similar potentials<sup>38</sup> for Ag, Zn, and Cd are suspect because they do not change sign with  $\Delta Z$ , the valence difference between solute and solvent, and hence can not resemble the usual electrostatic potentials at close approach. Our own efforts to use a quite reasonable oscillating potential, that of March and Murray, <sup>39</sup> gave in fact the wrong sign for  $\Delta Q$  for  $\Delta Z = 1$ , primarily because  $\frac{11}{16}d$  falls in a region little affected by the oscillations.

We wish to make two points in this regard. First that  $\frac{11}{16}d$  is really much too close to use the usual asymptotic form for the oscillating potential,<sup>35</sup>

$$V(r) = \frac{ed_0}{4k_t^2} \frac{\cos(2k_f r + \phi)}{r^3} , \qquad (27)$$

except perhaps for those cases such as the transition metals<sup>37,38</sup> where  $\phi$  is large and positive. In the second place the whole treatment of the semivacancies is now somewhat outmoded by the advent of the pseudopotentials to which Eq. (27) is closely related. Such treatments hinge primarily on central forces between actual atoms, at least as far as the second-order expansion of the pseudo-

Potential	φ	$\Delta H_m$	$\Delta H_f$	$\Delta Q^{a}$	$\Delta Q^{a}$ (semivacs) -4 eV(11d/16)
March and Murray (Ref. 39)		2.38	0.09	2.47	-6.33
Asymptotic form of oscil-					
lating potential [Eq. (27)]	0.10	10.16	-1.21	8.95	-3.60
	1.00	2.64	-0.05	2.59	- 0.26
	2.00	-3.58	1.11	-2.47	+3.55

TABLE III. Estimates of migration and formation energies for impurity  $(\Delta Z = 1)$  diffusion in tin (all in units of kcal/mole).

<sup>a</sup>These values are to be compared with the experimental value for antimony,  $\Delta Q = +3.5 \text{ kcal/mole}$ .

potential is concerned. While the behavior of the exchange and correlation terms in the neighborhood of the semivacancies may introduce small corrections, it seems pretty clear that the principal contribution to  $\Delta H_m$  can be taken from the difference of the two-body pseudopotential interactions for saddle and equilibrium configurations.

We have carried out just such a program for diffusion in tin, using two types of potential. One of these is the potential originally developed by March and Murray.<sup>39</sup> The other is variations of the oscillating potential used by Blandin and Deplante<sup>40</sup> in its asymptotic form, Eq. (27). In any serious attempt to apply such a potential one should attempt to determine the adjustable constants  $\alpha_0$ and  $\phi$  empirically-from Knight shift and incremental resistivity, for example. Lacking such data, we simply chose arbitrarily to put  $\alpha_0 = 1$  and took for  $\phi$  the three values of 0.1, 1.0, and 2.0 radians with  $\Delta Z = 1$  in mind. The results for  $\Delta H_f$ and  $\Delta H_m$  are given in columns three and four of Table III. The values for  $\Delta H_f$  are just the changes in energy which result when an impurity with a heterovalent charge (Z = 5) adjoins a vacancy.

The migration energies are calculated simply as the differences of the sums of the two-body interactions at the saddle-point position minus those at the equilibrium position. For the  $\Delta Q$  shown in the fourth column the sums of  $\Delta H_m$  and  $\Delta H_f$  appear because  $\Delta Q$  is positive for  $\Delta Z = +1$  judging from the diffusion of Sb in Sn and hence C is near zero. The experimental value of  $\Delta Q$  for this system is + 3.5 kcal/mole, which is to be compared with column four. One sees that the March and Murray potential gives the sign and order of magnitude of the experiment. The results from the asymptotic form of the oscillating potential depend sensitively on  $\phi$  but clearly include the experimental value in their range for small  $\phi$ . In the last column are the values of  $\Delta Q$  calculated the old way using the semivacancy concept. The results give the wrong sign for March and Murray potential and for the oscillating potential are significantly different, giving agreement with experiment only at large  $\phi$ . If one considers  $\Delta Z = -1$ ,  $\Delta Q$  is negative and appreciably smaller in magnitude. The correlation coefficient is here more important and tends, as always, to reduce  $|\Delta Q|$  through  $\Delta C$ .

These results do, we feel, bear out qualitatively the points stressed three paragraphs earlier. It is important, however, to point out that this model used to correlate substitutional diffusion with valence is essentially very crude and omits all details of band structure of the bulk metal and all perturbation of the lattice caused by the presence of the defects. Also there are clearly very important differences between isoelectric impurities, e.g., Zn and Cd, which must have a different origin such as ion size as mentioned earlier.

It is natural to ask how would the good agreement previously determined for the monovalent and some divalent solvents for  $\Delta Q$  with the semivacancy calculations be disturbed by using instead the technique presented here for  $\Delta H_m$ . In particular, one would tend to consider the interactions at closer distances between the moving and "ring" atoms. Any interaction potential based on electrostatic or band-structure considerations would give larger  $\Delta Q$  for larger  $\Delta Z$  and hence disturb the agreement generally. The effect of these interactions has been generally disregarded in the past. There is some reason to continue to do so on the basis that size consideration is also important for the interaction with the ring atoms and larger  $\Delta Z$  means smaller ion size. Perhaps this influence may roughly compensate the electrostatic effect from  $\Delta Z$  and thereby justify the customary neglect of these interactions. In the tin lattice, at least, there are essentially no "ring" atoms inhibiting vacancy jumping. In general the interaction of the moving atom with its neighbor at its original equilibrium position will play the role of the old semivacancy terms in that their influence will be to make  $\Delta H_m$  decrease as  $\phi$  increases.

Concerning the rapid diffusion of monovalent and divalent impurities in the tin lattice by the interstitial mechanism there appears to be one phase of the problem that has been largely overlooked in the past. It concerns the path of the interstitial down the tetragonal direction where large straight tunnels of considerable size are available. It appears that motion along these paths must be practically without activation energy in the usual sense. That is, the impurity is practically at neutral equilibrium. The wideness of tunnels is not the main argument for this conclusion. The main argument rests on the geometry of the tunnels themselves which possess a screw axis symmetry of  $2\pi/4$ . As a result an impurity moving a lattice translational distance c along the tetragonal axis will pass through three intervening equilibrium positions, or the effective jump distance in this direction is cut by a factor of 4. It is reasonable to conclude that the activation barrier is correspondingly reduced by roughly  $\frac{1}{16}$  under what one might otherwise expect and so would fall in the general range of thermal energies. It follows that the low activation energies observed for diffusion down the c axis would in this model be attributed to the energy to bring the impurity from a substitutional to an interstitial site. It is reasonable that the impurity might still interact strongly with the atoms of the tunnel, possibly by drawing them inward, more likely by pushing them outward. The mobility of the impurity would be impeded, not by the lattice structure, but by the self-trapping potential of its neighbors. The motion down the tunnel is then not in steps but in an unactivated, highly cooperative process involving the partially synchronized motion of many atoms. This model would appear to explain the low isotope effect found by Miller et al.<sup>41</sup> for the motion of Ag along the c axis in tin.

9

While the case for some sort of interstitial migration for zinc and the noble metals in tin seems quite well established at this time, there are additional experiments using hydrostatic pressure, isotope effect, internal friction, and electromigration that could be brought to bear for further clarification.

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### CONCLUSIONS

In addition to the quantitative results listed in Table I the following points have been stressed in this paper.

(a) Antimony and cadmium have been shown to be slow diffusers in tin, presumably moving substitutionally by the vacancy mechanism. Zinc is a fast diffuser like the noble metals in tin. No doubt an interstitial mechanism of some sort is responsible. The difference in behavior between zinc and cadmium can be attributed perhaps to the smaller size of the zinc ions.

(b) Of the slow diffusers those with the higher valence generally diffuse slower in contrast with the prevailing behavior for impurity diffusion in monovalent and divalent solvents. Some basis for understanding this correlation seems possible in terms of the oscillating potential model for the impurity if one calculates  $\Delta H_m$  somewhat differently than has been done in the past, i.e., by calculating energies through two-body interactions between atoms and neglecting the hemispherical vacancies which have generally played an important role up to now.

(c) Interstitial diffusion down the c axis in tin is facilitated no doubt by the large open "chimneys" in that direction. Even more interesting is the screw symmetry property down the chimney. As a result there must be four equilibrium positions along the chimney axis in any unit cell, so that the activation for motion in this direction can hardly exceed the thermal energies in the diffusion regime.

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