

# Diffusion of Cadmium, Indium, and Tin in Single Crystals of Silver\*†

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The diffusion coefficient of cadmium, indium, and tin tracers in single crystals of pure silver has been measured as a function of temperature over the range 592–937°C. The activation energies and frequency factors were determined, yielding  $D=0.44 \exp(-41\,700/RT)$  for the cadmium tracer,  $D=0.41 \exp(-40\,630/RT)$  for indium, and  $D=0.25 \exp(-39\,300/RT)$  cm<sup>2</sup>/sec for tin. These values are in marked disagreement with the older data. The results of the present work are discussed in terms of Lazarus' theory and Zener's theory. Both theories give fair agreement with the experimental data.

## INTRODUCTION

IT has long been noted that the activation energy for chemical diffusion, i.e., the diffusion of impurities, is often exceedingly smaller than that for self-diffusion in the matrix metal.<sup>1</sup> A similar difference is seen in the values of the frequency factor. Theoretical efforts have been made in the past either to explain this effect<sup>1,2</sup> or to suggest the re-examination of the experimental results.<sup>3–5</sup> The latter approach finds more justification in view of the questionable accuracy of much of the old data.<sup>6</sup> In the first place, in most of the old experiments there was a concentration gradient which was not negligible and hence could have caused large unidirectional currents of imperfections as are seen in Kirkendall effect. Secondly, most of the experiments were carried out on polycrystalline specimens. As was shown by Fisher,<sup>7</sup> Hoffman and Turnbull,<sup>8</sup> Slifkin, Lazarus, and Tomizuka,<sup>9</sup> and Wajda,<sup>10</sup> diffusion along grain boundaries can mask the volume diffusion, especially at low temperatures. Moreover, the availability in recent years of radioactive isotopes of high specific activity has made it possible to obtain considerably greater accuracy in diffusion measurements than previously.

It thus seems evident that the redetermination of the activation energies and the frequency factors for chemical diffusion is necessary. The work reported here satisfies the following conditions: (1) Experiments were

carried out on a pure metal and with an extremely dilute solute concentration, by the use of high specific activity radioisotopes. (2) Carefully grown single crystals were employed. (3) A monovalent face-centered cubic metal was chosen for the matrix crystal for ease of theoretical treatment. (4) The elements to be diffused into the metal were chosen in a systematic manner, as those neighboring the matrix metal in the periodic table. (5) Isotopes of long half-life were used to minimize errors. Silver is seen to be quite convenient as a solvent metal. In addition to the availability of high-purity silver, self-diffusion in pure silver has been studied by three independent groups of investigators<sup>8,9,11</sup> with satisfactory agreement in their results. Moreover, the neighboring elements, cadmium, indium, tin, etc., have isotopes of long half-life.

It is hoped that the present determination of the activation energy and the frequency factor as a function of the atomic number of the diffusing elements will be significant in re-appraising the existing theories and will contribute to an adequate understanding of the mechanisms involved in diffusion in metals. The results of the first stage of this general program of investigation have been reported previously.<sup>12</sup>

## EXPERIMENTAL

Specimens were prepared from Handy and Harmon silver of 99.99 percent purity. Single crystals were grown in high-purity graphite crucibles in a vacuum furnace with a temperature gradient.<sup>13</sup> Crystals thus grown were etched, cast in plaster, cut into the form of short cylinders, polished mechanically and electrolytically, and annealed to remove any residual strains. They were then etched again to ascertain their monocrystallinity. Acceptable specimens were electroplated on their ends with high specific activity processed radio-isotopes obtained from Oak Ridge National Laboratory. The following plating baths were found to be practical: cadmium-115 (available as a nitrate in acid solution):

<sup>11</sup> W. A. Johnson, Trans. Am. Inst. Mining Met. Engrs. **143**, 107 (1941).

<sup>12</sup> Sonder, Slifkin, and Tomizuka, Phys. Rev. **93**, 970 (1954); Slifkin, Lazarus, and Tomizuka, J. Appl. Phys. **23**, 1405 (1952).

<sup>13</sup> D. Lazarus and D. R. Chipman, Rev. Sci. Instr. **22**, 211 (1951).

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<sup>1</sup> R. P. Johnson, Phys. Rev. **56**, 814 (1939); F. Seitz in *Phase Transformations in Solids*, edited by R. Smoluchowski *et al.* (John Wiley and Sons, Inc., New York, 1951).

<sup>2</sup> G. J. Dienes, Phys. Rev. **89**, 185 (1953).

<sup>3</sup> C. Zener, J. Appl. Phys. **22**, 372 (1951); C. Zener, in *Imperfections in Nearly Perfect Crystals*, edited by W. Shockley *et al.* (John Wiley and Sons, Inc., New York, 1952).

<sup>4</sup> A. S. Nowick, J. Appl. Phys. **22**, 1182 (1951).

<sup>5</sup> A. D. LeClaire, Acta Metallurgica **1**, 438 (1953).

<sup>6</sup> W. Seith and E. Peretti, Z. Elektrochem. **42**, 570 (1936). Tabulations of data are seen in W. Jost, *Diffusion in Solids, Liquids, Gases* (Academic Press, Inc., New York, 1952).

<sup>7</sup> J. C. Fisher, J. Appl. Phys. **22**, 74 (1951).

<sup>8</sup> R. E. Hoffman and D. Turnbull, J. Appl. Phys. **22**, 634 (1951).

<sup>9</sup> Slifkin, Lazarus, and Tomizuka, J. Appl. Phys. **23**, 1032 (1952).

<sup>10</sup> E. S. Wajda, Acta Metallurgica **2**, 184 (1954).

$\text{Cd}(\text{NO}_3)_2$  radioactive, 0.005*N*; KOH, to make the bath slightly basic (*pH* 9–10); KCN, 1.5*N*; with a cadmium anode. Indium-114 (available as an irradiated unit or as a chloride in acid solution):  $\text{In}_2(\text{SO}_4)_3$  radioactive, 0.01*N*;  $\text{Na}_2\text{SO}_4$ , 0.1*N*; with an indium and platinum anode. Tin-113 (available as a chloride in acid solution):  $\text{SnCl}_2$  radioactive, 0.004*N*;  $\text{NaHC}_4\text{H}_4\text{O}_6$ , 12*N*; NaOH, 0.004*N*; with a zinc anode. A cyanide bath similar to the cadmium plating bath was initially employed for the plating of indium but was discontinued after three specimens were plated due to the instability of the solution. The current density ranged between 8 and 40 ma/dm<sup>2</sup> and the estimated thickness of the plated layer ranged from 10 Å to 100 Å.

Electroplated specimens were sealed off in evacuated Vycor tubes and placed in controlled furnaces. Furnaces operating at temperatures below 700°C were controlled by an ac resistance bridge with a platinum winding as one arm. To stabilize the operation of the controllers, a motor-driven switch was inserted to cut off the plate voltage of the thyatron momentarily every one-half minute to quench the arc. The furnaces operating at temperatures above 700°C were controlled by Tag Celestrays. In either case the temperature at the specimen was held constant within  $\pm 0.5^\circ\text{C}$  over the entire period of diffusion anneal which ranged from several hours to three months, depending on the temperature.

Sectioning was performed on a precision lathe with a specially designed chuck which permitted a wide adjustment of the specimen orientation relative to the lathe axis. In order to eliminate effects of surface diffusion, a thickness of approximately  $6(Dt)^{1/2}$  was removed from the side before sectioning, where *D* is the estimated diffusion coefficient and *t* the time of anneal. In sectioning, the thickness of each cut varied from one-half mil to a few mils depending on the depth of penetration of the diffused isotope. The zero setting of the dial indicator used in the measurement of depth was determined by electrically insulating the cutting tool and determining the point of electrical contact between the tool and the surface of the specimen.

Each cut from a specimen was assayed by an immersion-type beta counter (N. Wood Counterlab type B, wall thickness 30 mg/cm<sup>2</sup>). The counting vessel consisted of a graduated cylinder, a Teflon adaptor at the bottom of the cylinder which served to expel radioactive acid solution from the dead portion of the counter and to hold the bottom tip of the counter tightly, and a Lucite ring at the open end of the cylinder for the centering of the counter. There were markers on the cylinder, the Teflon adaptor and the counter, and adjustments were made before each counting so that the markers all coincided. These precautions were employed to insure reproducibility of the counting geometry. In order to eliminate possible differences in the absorption caused by the variation in the density of the solution from one cut to the other, 10-mil silver wire of commercial purity was added to normalize the density. The assaying of the

specimens with  $\text{Sn}^{113}$  isotope was started at least two days after the specimen was taken out of the furnace so that no part of the diffusion of its radioactive daughter  $\text{In}^{113}$  (1.7 hours half-life) was measured.

To determine the distance accurately, weights of all cuts except the first one at the original surface were added and the mass equivalent of distance was calculated by assuming that the over-all dial-gauge reading of the distance between the front face of the second cut and the end of the last cut was correct. This factor was used to recalculate the center of each cut, including the first. The dial-gauge reading of the depth of the first cut is less reliable because the surface of the specimen is not ideally flat and the point of electrical contact does not always coincide with the zero-point of mechanical cutting.

The above procedure was repeated throughout the entire series of experiments except for one case, diffusion of In at 613°C, where the sectioning was performed<sup>14</sup> on a specially designed precision grinding machine.<sup>15</sup>

## RESULTS

A total of 18 diffusion runs were performed, six on each diffusing element, covering the temperature range 592–937°C. Results plotted in Figs. 1–3 show that the specific activity of cuts falls off exponentially as the square of the penetration depth. This fact, as well as the observations of the results of etching the remainders of

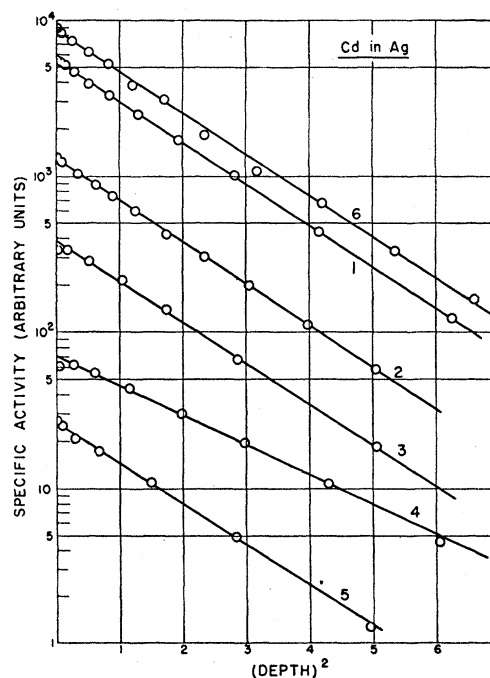


Fig. 1. Penetration curves for diffusion of Cd in Ag. See Table I for the scaling factors for the distance.

<sup>14</sup> Cooperation of Dr. H. Letaw, Jr., is gratefully acknowledged.

<sup>15</sup> Letaw, Slifkin, and Portnoy, *Phys. Rev.* **93**, 892 (1954); also *Rev. Sci. Instr.* (to be published).

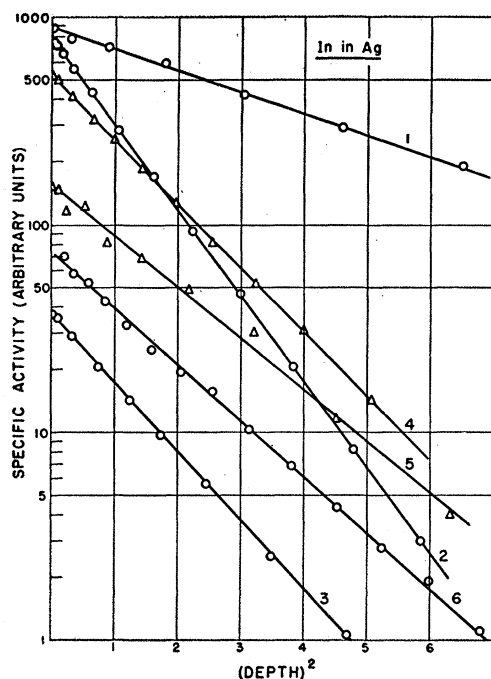


FIG. 2. Penetration curves for diffusion of In in Ag. See Table II for the scaling factors.

the specimens, indicates that there was no observable grain-boundary diffusion taking place due to an accidental recrystallization during the diffusion anneal.

Diffusion coefficients obtained from the penetration curves, temperatures, scaling factors for all the plots in

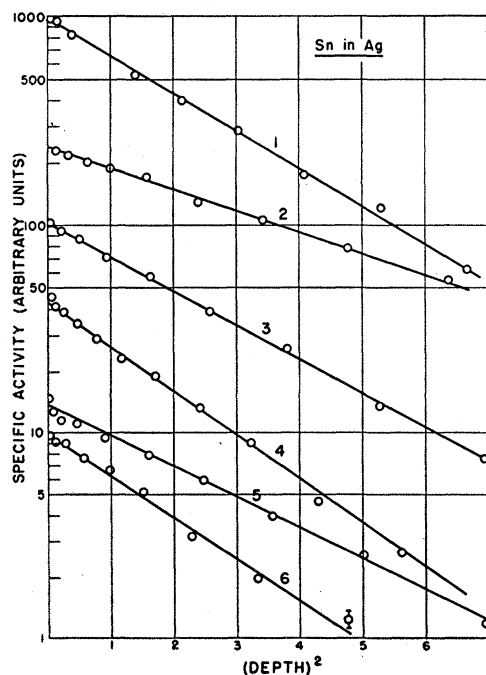


FIG. 3. Penetration curves for diffusion of Sn in Ag. See Table III for the scaling factors.

TABLE I. Diffusion of cadmium in silver.

Curve	Unit of (depth) <sup>2</sup> (cm <sup>2</sup> )	Temperature (deg C)	Time (sec)	<i>D</i> (cm <sup>2</sup> /sec)
1	$2.00 \times 10^{-3}$	936.8	$6.39 \times 10^4$	$1.28 \times 10^{-8}$
2	$1.29 \times 10^{-3}$	862.5	$1.25 \times 10^5$	$4.18 \times 10^{-9}$
3	$6.45 \times 10^{-4}$	758.8	$3.97 \times 10^5$	$6.74 \times 10^{-10}$
4	$3.87 \times 10^{-4}$	724.0	$6.59 \times 10^5$	$3.25 \times 10^{-10}$
5	$1.29 \times 10^{-4}$	651.7	$9.47 \times 10^5$	$6.06 \times 10^{-11}$
6	$2.15 \times 10^{-4}$	592.3	$7.06 \times 10^5$	$1.25 \times 10^{-11}$

Figs. 1-3, and the time of diffusion anneal are given in Tables I-III. Figure 4 represents the data plotted as  $\log D$  versus  $1/T$ , where  $T$  is the absolute temperature. The best least-squares straight lines are given by the equations

$$D_{Cd} = 0.44 \exp(-41\,700/RT),$$

$$D_{In} = 0.41 \exp(-40\,630/RT),$$

$$D_{Sn} = 0.25 \exp(-39\,300/RT),$$

where the subscripts on  $D$  indicate the solute and  $R$  is the gas constant. Also shown in Fig. 4 are the results of self-diffusion<sup>9</sup> and diffusion of antimony in silver<sup>12</sup> which are given by the equations

$$D_{self} = 0.724 \exp(-45\,500/RT),$$

and

$$D_{Sb} = 0.169 \exp(-38\,320/RT).$$

These data and the results of the present measurements are tabulated in Table IV where all  $D_0$ 's are normalized for the mass number 110 by multiplying by the factor (mass of isotope/110)<sup>1/2</sup>, thus eliminating the difference in jump frequencies due to different isotope masses.

The activation energy  $H$  is plotted as a function of the atomic number (i.e., excess valence  $Z$ ) in Fig. 5. If the value for self-diffusion is excluded, the activation energies are described by the expression:  $H$  (in kcal/mole) =  $42.8 - 1.13 Z$ .

Each diffusion coefficient is accurate to about  $\pm 2$  percent. This precision, the number of measurements and the temperature range determine the activation energy  $H$  and the frequency factor  $D_0$ , approximately within  $\pm 0.5$  percent and  $\pm 10$  percent, respectively.

## DISCUSSION OF THE RESULTS

The present results differ radically from the earlier measurements made on the same system by Seith and Peretti.<sup>6</sup> These workers reported the activation energy

TABLE II. Diffusion of indium in silver.

Curve	Unit of (depth) <sup>2</sup> (cm <sup>2</sup> )	Temperature (deg C)	Time (sec)	<i>D</i> (cm <sup>2</sup> /sec)
1	$6.45 \times 10^{-4}$	936.0	$4.17 \times 10^4$	$1.73 \times 10^{-8}$
2	$1.94 \times 10^{-3}$	860.8	$8.64 \times 10^4$	$5.89 \times 10^{-9}$
3	$6.45 \times 10^{-4}$	760.0	$2.36 \times 10^5$	$8.95 \times 10^{-10}$
4	$6.45 \times 10^{-4}$	715.8	$6.05 \times 10^5$	$3.85 \times 10^{-10}$
5	$3.23 \times 10^{-4}$	661.3	$1.36 \times 10^6$	$1.30 \times 10^{-10}$
6	$2.67 \times 10^{-5}$	612.7	$3.14 \times 10^6$	$3.44 \times 10^{-11}$

TABLE III. Diffusion of tin in silver.

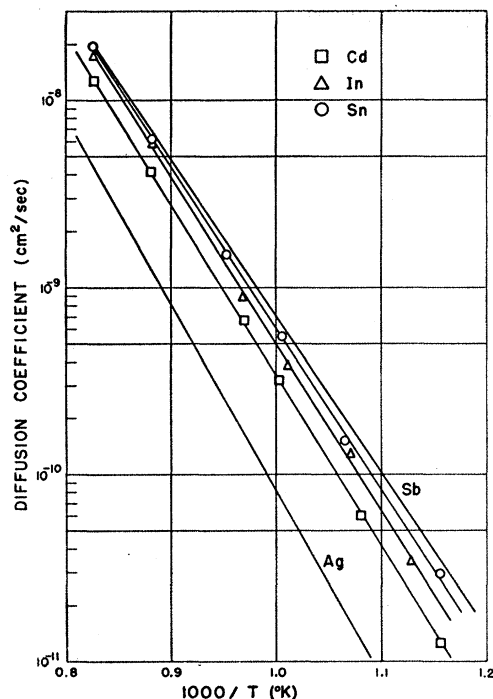
Curve	Unit of (depth) <sup>2</sup> (cm <sup>2</sup> )	Temperature (deg C)	Time (sec)	<i>D</i> (cm <sup>2</sup> /sec)
1	$1.29 \times 10^{-3}$	937.0	$3.96 \times 10^4$	$1.97 \times 10^{-8}$
2	$6.45 \times 10^{-4}$	860.8	$9.36 \times 10^4$	$6.20 \times 10^{-9}$
3	$5.00 \times 10^{-4}$	776.0	$2.21 \times 10^5$	$1.50 \times 10^{-9}$
4	$6.45 \times 10^{-4}$	722.0	$5.83 \times 10^5$	$5.51 \times 10^{-10}$
5	$2.58 \times 10^{-4}$	666.3	$1.21 \times 10^6$	$1.51 \times 10^{-10}$
6	$2.58 \times 10^{-4}$	592.3	$4.75 \times 10^6$	$2.97 \times 10^{-11}$

to be 22.35, 24.4, and 21.4 kcal/mole and  $D_0$  to be  $4.9 \times 10^{-5}$ ,  $7.3 \times 10^{-5}$ , and  $7.8 \times 10^{-5}$  cm<sup>2</sup>/sec for the diffusion in silver of cadmium, indium, and tin, respectively. In the present work the extreme difference in activation energy and the frequency factor between self-diffusion and chemical diffusion is considerably reduced. The discrepancy between the present results and the older ones cannot be solely due to the existence of grain-boundary diffusion in the old measurements, since the recent determination of the diffusion of antimony in polycrystals of silver<sup>12</sup> agrees with measurements on single crystals except for temperatures below 600°C, where the effect of grain boundaries becomes significant. The existence of still some other short-circuiting paths, as suggested by Zener<sup>3</sup> and Nowick,<sup>4</sup> to explain the low values of the activation energy in the old data seems unwarranted, since in the high-temperature region of the range of measurement the old values of the diffusion coefficient are substantially less than the corresponding values given by the present work. It is possible that the discrepancy was caused by the presence of an appreciable concentration gradient, since the old measurements involved the use of a diffusion couple which consisted of a 2 percent alloy and a pure silver crystal. It is not obvious, however, that the discrepancy is explainable by the flow of unidirectional vacancy currents alone. The possible variation of the diffusion coefficient along the diffusing path, the Kirkendall shift, and the lack of more accurate means of measurement all combined together could very likely have been the reason for the disagreement. Examination of the old data reveals that some of the plots of  $\log D$  versus  $1/T$  were not linear but possessed a knee which would subject the accuracy of the measurement itself to some question.

In the light of the present results, it seems imperative that most of the existing data on chemical diffusion

TABLE IV. Diffusion in silver.

Isotope	Experimental activation energy (cal/mole)	Frequency factor (normalized) (cm <sup>2</sup> /sec)	$D_0$ , Zener (cm <sup>2</sup> /sec)	$H$ , Nowick (cal/mole)	Screen- ing con- stant $q$ (1/Å)	$D_0$ , calcu- lated from $q$ , (cm <sup>2</sup> /sec)
<sup>107</sup> Ag	45 500	0.724	0.724	44 900	1.725 <sup>a</sup>	...
<sup>115</sup> Cd	41 700	0.454	0.462	41 720	1.55	0.39
<sup>113</sup> In	40 630	0.416	0.416	40 770	1.67	0.28
<sup>113</sup> Sn	39 300	0.255	0.364	40 370	1.70	0.22
<sup>124</sup> Sb	38 320	0.179	0.331	40 160	1.74	0.16

<sup>a</sup> N. F. Mott, Proc. Cambridge Phil. Soc. 32, 281 (1936).FIG. 4. Diffusion data plotted as  $\log D$  versus  $1/T$ .

which show substantial differences in their values of  $H$  and  $D_0$  as compared with the values for self-diffusion be re-examined as a basis for theoretical considerations on chemical diffusion at extremely dilute concentrations. Before accepted, these measurements should be repeated by using high-specific activity radio-isotopes at extremely low solute concentrations and negligible concentration gradients.

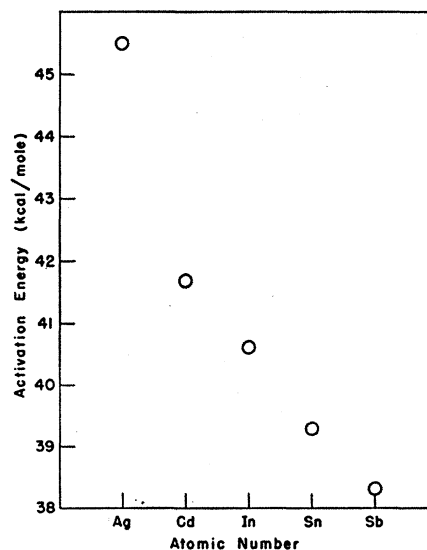


FIG. 5. Activation energy for diffusion in silver plotted as a function of atomic number.

It is obvious that there are significant differences in the rate of diffusion of the various solute atoms and that of the solvent. Speculation by LeClaire<sup>5</sup> that these differences would vanish at sufficiently small solute concentrations seems to be unfounded. The solute concentrations in the present work were of the order of  $10^{-4}$  to  $10^{-5}$  which is within the range of purity of the 99.99 percent silver used in the experiment. This estimation is based on the thickness of the plated layer and the penetration distance.

The comparatively small difference in activation energy indicates that the binding energy between a solute atom and a vacancy is much less than previously considered by Johnson<sup>1</sup> on the basis of the old data. The atomistic approach of Lazarus,<sup>16</sup> which yielded good agreement with the silver-antimony data<sup>12</sup> offers a reasonable basis for the explanation of the present results. Assuming a fixed screening constant  $q$ , which is determined from Poisson's equation and is not considered an adjustable parameter and using the observed  $H$  and  $D_0$  for silver self-diffusion, calculations are made of  $H$  and  $D_0$  for solute diffusion, the results of which are represented along with the experimental results in Fig. 6. Though  $q$  is rigidly held constant in the Thomas-Fermi approximation, it may be expected to vary in actual cases as is discussed below. The results of the present work may thus be used as a means of estimating corrections to the screening constant, since all other quantities are known. Lazarus' relation gives  $\Delta H/Z$  as a function of  $q$ , where  $\Delta H = H(\text{solvent}) - H(\text{solute})$  and  $Z$  is the excess valence. The experimental values of  $\Delta H/Z$  thereby determine  $q$  for each solute. These values and the values of  $D_0$  calculated by using these experimentally determined screening constants are listed in Table IV. The value of  $q$  varies by 10 percent for  $Z$  ranging from 1 to 4, which is consistent with the approximation employed in the theory. Recent calculations by Friedel<sup>17</sup>

show that the Thomas-Fermi model is not correct for small odd values of  $Z$ . It was shown that in addition to the first valence electrons which are lost to the conduction band, possibly a fraction of a second valence electron of some di- or tetravalent impurities may not be retained in bound states when the matrix is a noble metal. In terms of this view, the present results indicate that such an effect, as in the case of divalent cadmium, results in a smaller value of  $q$ . If the case of cadmium be excepted, then the value of  $q$  is constant to within  $\pm 2$  percent, which gives justification to the model employed in the screening theory. As a further check on the theory of the diffusion in silver, tracers of the elements preceding silver in the periodic table should be studied. A measurement of the diffusion of ruthenium in silver is now under way in this laboratory by using Ru<sup>103</sup> isotope and the preliminary results indicate the activation energy to be considerably larger than that for self-diffusion in silver. This agrees qualitatively with the screening theory.

According to Zener,<sup>3</sup>  $D_0$  can be estimated from the values of  $H$  by the relation

$$D_0 = a^2 \nu \exp(\lambda \beta H / RT_m),$$

where  $a$  is the lattice constant,  $\nu$  the vibrational frequency,  $\lambda$  a numerical constant often taken to be 0.55 for f.c.c. metals,  $T_m$  the melting point, and  $\beta$  a constant related to the shear modulus  $\mu$  by the relation  $\beta = d(\mu/\mu_0)/d(T/T_m)$ . In very dilute solution all of these quantities except  $\nu$  and  $H$  are those of the solvent metal. An estimation of  $D_0$  was made by approximating  $\nu$  by the Debye frequency of silver and by using the experimentally determined values of  $H$ . The term  $\beta$  was taken to be 0.45, and  $\lambda$  to be 0.54 to normalize the results to the measured values for self-diffusion. The results are given in Table IV along with the estimation of  $H$ , which

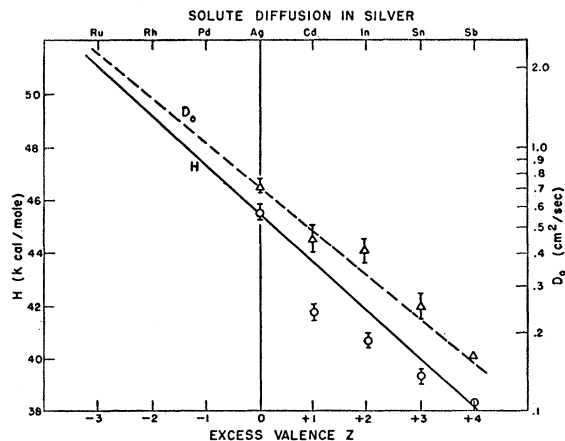


FIG. 6. Theoretical plots of  $H$  and  $D_0$  compared with the experimental data.

<sup>16</sup> D. Lazarus, Phys. Rev. **93**, 973 (1954).

<sup>17</sup> J. Friedel, Phil. Mag. **43**, 153 (1952).

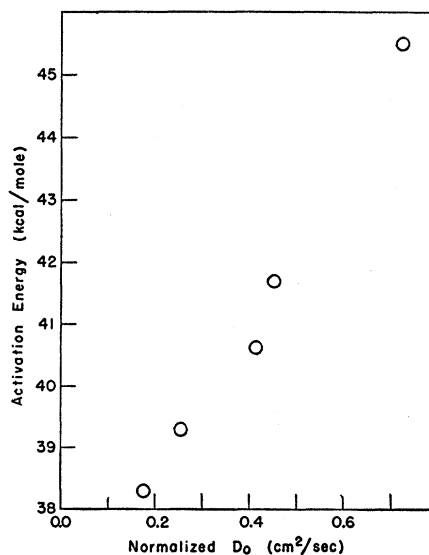


FIG. 7. Plot of  $H$  against  $D_0$ .

is obtained by using only the diffusion coefficients at the highest temperature for all the isotopes and employing Zener's theory as was suggested by the work of Nowick.<sup>4</sup> The values of  $H$  and  $D_0$  thus calculated yield excellent agreement with the experimental results for cadmium and indium but significant deviations are seen for tin and antimony. Moreover, they do not reproduce the experimental correlation between  $H$  and  $D_0$  which is shown in Fig. 7. Perhaps this discrepancy results from our use of a constant value of  $\nu$ . It should be noted that Zener's theory shows better agreement with experiment for smaller values of  $Z$  where the activation energies predicted by the screening theory deviate appreciably and the situation is reversed for cases of larger  $Z$ . It may

be that an appreciable portion of the free energy is expended in the changing of configurations other than the straining of the lattice (e.g., the redistribution of the electronic charge) when a relatively large number of extra electrons are attached to the impurity atoms, and that the assumption of Zener's theory is thus violated.

The negative values for the entropy of activation, which were implied by the old data and have been subject to much theoretical speculation, are not observed in the present work and their notion, in all probability, must be discarded for the case of dilute chemical diffusion in f.c.c. metals.

The authors wish to express their gratitude to Dr. F. Seitz and Dr. D. Lazarus for many helpful discussions.

## Shapes of Absorption and Emission Lines of Impurities in Solids\*

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Existing treatments of band shapes in solids, for the simplest impurity centers, predict Gaussian shape functions. These treatments assume for simplicity that the electronic matrix element is independent of the nuclear wave functions, and that the energy width of the band is negligible compared with the energy of the mid-point of the band. We estimate here the expected magnitude of the effect of correcting these assumptions in typical cases, and find that the emission or absorption band may deviate from a Gaussian by twenty percent or more on the wings.

**A**BSORPTION and emission spectra are not generally of a simple shape for several possible reasons. In the simplest case, where only a single initial electronic state and a single final electronic state can contribute to the line, where the environment of all the centers is identical, where the transition is far from resonance with the host lattice, and where the configurational coordinate curve for the final electronic state is sufficiently displaced from that for the initial state, an approximate calculation leads to a Gaussian shape function for the absorption or emission spectrum.<sup>1-4</sup> This result depends on the Born-Oppenheimer approximation and on the assumption that the electronic transition probability is independent of the nuclear wave functions, i.e., the wave functions for the lattice vibrations. This assumption is generally made in three parts: (1) the wave function of only one electron is changed during the transition, (2) the electronic matrix element for this one electron is independent of the nuclear wave functions, and (3) the width of the

band is negligible as compared with the energy of its mid-point. On configurational coordinate diagrams these assumptions are equivalent to assuming that the electronic transition probability is independent of the configurational coordinate, so that line shapes are determined solely by the geometry of the energy curves.

The purpose of this note is to point out the influence of these approximations upon the calculated line shape. For simplicity and ease of presentation the description will be given in terms of the usual configurational coordinate model (in which the important coordinate is presumably the position of the nearest ions).

In case the ground and excited states are influenced by about the same relative amount<sup>5</sup> by the lattice oscillations, as may be true in a system such as KCl:Ti where both ground and excited state wave functions are relatively compressed, the electronic momentum matrix element is given by

$$\langle \mathbf{p} \rangle = \langle \mathbf{p} \rangle_0 (1 - \Delta R/R), \quad (1)$$

where  $R$  is any characteristic length in the wave functions of the center. As the neighbors of the center move and cause a change in the wave function, i.e., in  $R$ ,

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<sup>1</sup> M. Lax, *J. Chem. Phys.* **20**, 1752 (1952).

<sup>2</sup> F. E. Williams and M. H. Hebb, *Phys. Rev.* **84**, 1181 (1951).

<sup>3</sup> R. C. O'Rourke, *Phys. Rev.* **91**, 265 (1953).

<sup>4</sup> C. C. Klick, *Phys. Rev.* **85**, 154 (1952).

<sup>5</sup> By the phrase "the same relative amount" we mean the equality of the logarithmic differentials of the damping lengths of the two wave functions.