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Impurity Diffusion in Aluminum*

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The diffusion of ^{71}Ge, ^{72}Ga, ^{65}Zn, ^{64}Cu, ^{110}Ag, and ^{198}Au in aluminum single crystals has been measured by the tracer-sectioning technique. The diffusion coefficients, in cm^2/sec, are given by: $D_{\mathrm{Ge}}=0.481\exp[-(28{,}980\pm210)/RT]$, $D_{\mathrm{Ga}}=0.490\exp[-(29{,}240\pm141)/RT]$, $D_{\mathrm{Zn}}=0.259\exp[-(28{,}860\pm134)/RT]$, $D_{\mathrm{Cu}}=0.647\exp[-(32{,}270\pm270)/RT]$, $D_{\mathrm{Ag}}=0.118\exp[-(27{,}830\pm142)/RT]$, and $D_{\mathrm{Au}}=0.131\exp[-(27{,}790\pm240)/RT]$. Less extensive measurements of the diffusion of ^{60}Co and ^{51}Cr in aluminum are also reported. The activation energies obtained in this study cannot be reconciled with the large impurity-vacancy binding energies deduced from quenching studies; the difference is explained in terms of clustering effects in the quenching experiments. The difference between the present data and the low values of D_0 and Q for impurity diffusion in aluminum reported by Agarwala and co-workers can be explained by the effect of a surface oxide.

INTRODUCTION

THE primary objective of this study was to determine whether the electrostatic interaction theory,[1,2] which has been very successful in predicting values of the difference ΔQ between the activation energies for impurity- and self-diffusion for the diffusion of electropositive elements in copper and silver, can be applied to diffusion in aluminum. The theory is based on the model that an impurity of excess charge Z is dissolved in a metal and screened by the conduction electrons; it is the electrostatic interaction of the vacancy with this screened potential that is used to evaluate ΔQ. The Thomas-Fermi potential was used in previous work as the potential around the impurity; however, it seems desirable to use the more realistic oscillating potentials of March and Murray[3] for a polyvalent metal like aluminum. Our approach, then, is to determine accurate values of ΔQ for the diffusion of electropositive and electronegative impurities in aluminum, and to use these values to check both the applicability of the model to aluminum and the importance of the oscillations in the March-Murray potentials.

The second objective of our study was to resolve the controversy about the impurity-vacancy binding energy for certain solutes in aluminum. Numerous quenching studies[4] on dilute aluminum alloys have suggested large impurity-vacancy binding energies, whereas high-temperature equilibrium measurements[5] and calculations[6] based on the electrostatic interaction model have indicated very small binding energies. Since the binding energy is a term in ΔQ, experimental values of ΔQ may resolve this discrepancy.

Our third goal was to shed some light on the exceptionally low values of the preexponential terms (D_0's) and activation energies reported for the diffusion of many impurities in aluminum.[7–9]

EXPERIMENTAL

Single crystals were grown from 99.999%-pure aluminum by the Bridgman method. Diffusion samples 1 cm in diam and 1 cm long were spark cut from the single crystal, the ends of the sample were ground flat and parallel on a precision grinder, and the samples were given a light etch and annealed overnight at 600°C. After inspection for defects and for monocrystallinity, the samples were given a light etch and immediately placed in a vacuum evaporator for isotope deposition. One of the isotopes, ^{64}Cu, ^{65}Zn, ^{72}Ga, ^{71}Ge, ^{110}Ag, or ^{198}Au, initially in the metallic state, was evaporated from a tantalum boat onto the flat surface of the samples. The samples were placed in tantalum cups, sealed in quartz capsules evacuated to better than 2×10^{-5} Torr, and annealed for periods of several hours to several weeks at a temperature known to better than ±1°C.

After the diffusion anneal, the samples were reduced in diameter to eliminate edge effects by trepanning with a spark cutter, and were then sectioned on a microtome. The slices from each section were collected and weighed on a Mettler microbalance. The sum of the weights of the sections was within 1% of the difference in weight of the sample before and after sectioning. The thickness of each section was determined from the diameter and density of the specimen and the weight of the section.

The isotope concentration in each section, for all the isotopes except ^{71}Ge, was determined by counting the

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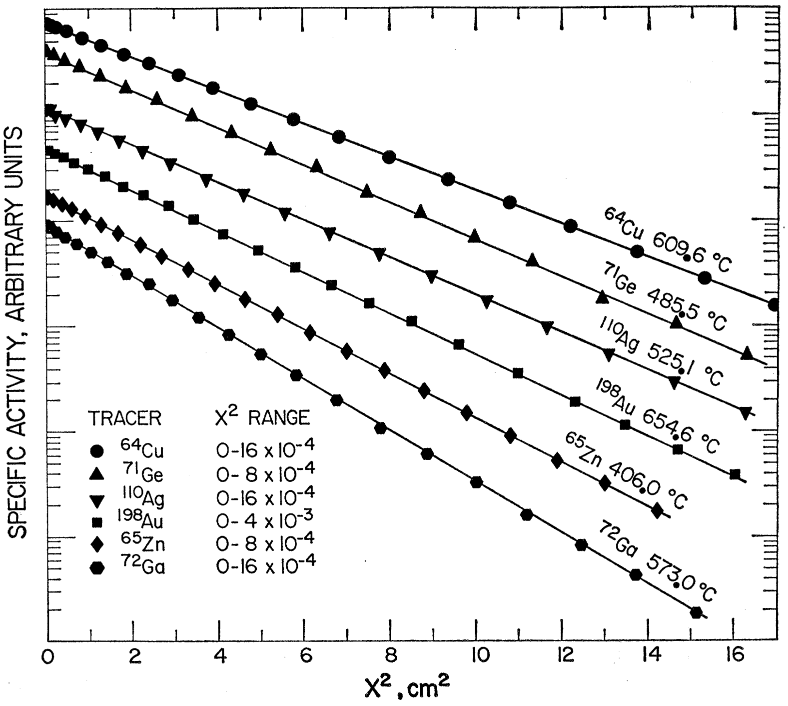

FIG. 1. Log specific activity versus penetration-distance squared for impurity diffusion in aluminum. The X^2 range indicated in the legend is the value of the range 0–16 on the abscissa.

emitted γ rays in a well-type scintillation counter. In order to count the Ga x ray emitted by ^{71}Ge, the aluminum slices from a section were attached to a counting planchet with double-sided tape and then counted in an end window flow proportional counter. Each section was counted to 10^4 or more counts above background.

RESULTS

The solution of the diffusion equation for the boundary conditions used in our experiments is

$$\ln C = \text{const} - X^2/4Dt, \qquad (1)$$

where C is the specific activity of the tracer in a section whose center is X-cm distant from the original surface, and t is the annealing time. Figure 1 shows a typical semilog plot of specific activity versus X^2 for each one of the tracers. The linearity of the plots over several orders of magnitude in specific activity shows that volume diffusion is being measured. The values of D are shown as a function of $1/T$ in Figs. 2 and 3 and are listed in Table I. The line in both Figs. 2 and 3, marked "29 kcal/mole," is drawn with a slope of 29 kcal/mole, and represents what we think are the best values for self-diffusion in aluminum, as discussed below. The parameters from a least-squares fit to the lines in Figs. 2 and 3 are given in Table II.[10]

DISCUSSION

Comparison with Literature—Nontransition-Metal Impurities

Our data are in excellent agreement with the recent data of Alexander and Slifkin[11] on the diffusion of copper, silver, and gold tracers in aluminum single crystals, and with the data of Heumann and Böhmer[12] on the diffusion of silver in aluminum, the values of D seldom differing by more than 5%. Good agreement is obtained with the data of Hilliard *et al.*,[13] on the diffusion of zinc in aluminum if their highest temperature points, which are significantly above their Arrhenius line, are dropped. The agreement with the data of Agarwala and co-workers on the diffusion of silver[8] and copper[14] in aluminum, and with the data of Badrinayaranan and Mathur[15] on the diffusion of silver in aluminum is only fair; however, these sets of data appear to be less reliable because the D's were obtained from penetration plots extending over less than a factor of 10 in specific activity, and their scatter on an Arrhenius plot is appreciable. The values of D_0 and Q reported for the diffusion of palladium,

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[10] The data in Fig. 2 was previously presented at the March APS Meeting 1967 (unpublished); N. L. Peterson and S. J. Rothman, Bull. Am. Phys. Soc. **12**, 324 (1967).

[11] W. Alexander and L. Slifkin (private communication); Bull. Am. Phys. Soc. **14**, 388 (1969).

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[15] S. Badrinarayanan and H. B. Mathur, Intern. J. Appl. Radiation Isotopes **19**, 353 (1968).

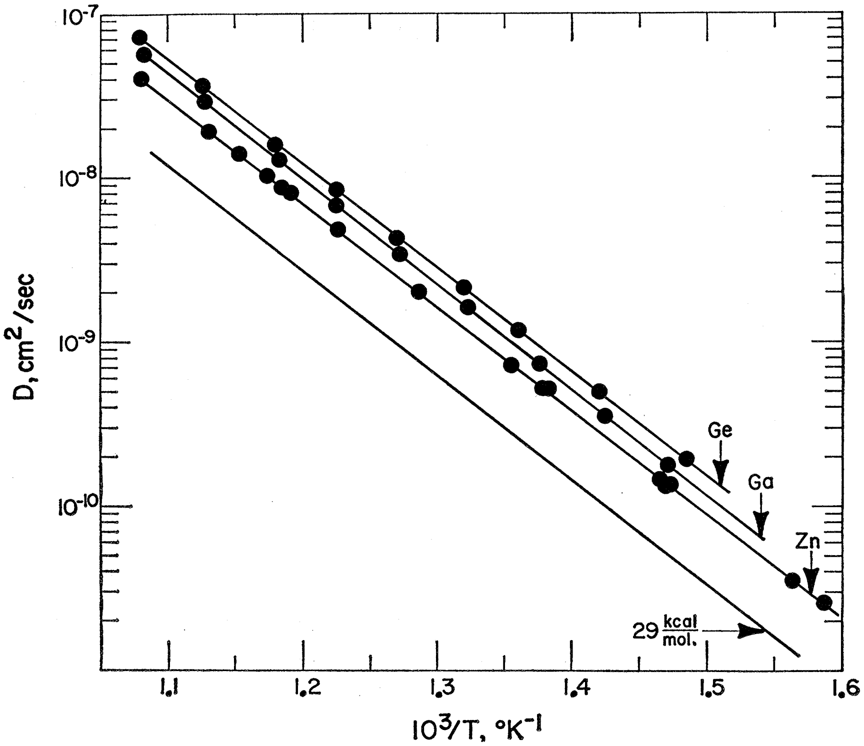

FIG. 2. $\log_{10} D$ versus reciprocal absolute temperature for germanium, gallium, and zinc diffusion in aluminum. The 29-kcal/mole line is common to both Figs. 2 and 3.

cadmium, indium, and tin in aluminum[8] are so much lower than our data that we believe they do not represent volume diffusion; this point is discussed later. We conclude that (1) measurements of diffusion in aluminum are made difficult by the oxide layer on aluminum. However, these difficulties can be overcome. (2) The nontransition-metal impurities gold, silver, copper, zinc, cadmium,[11] gallium, germanium, and antimony[15] diffuse in aluminum with activation energies between 28 and 30 kcal/mole, with the exception

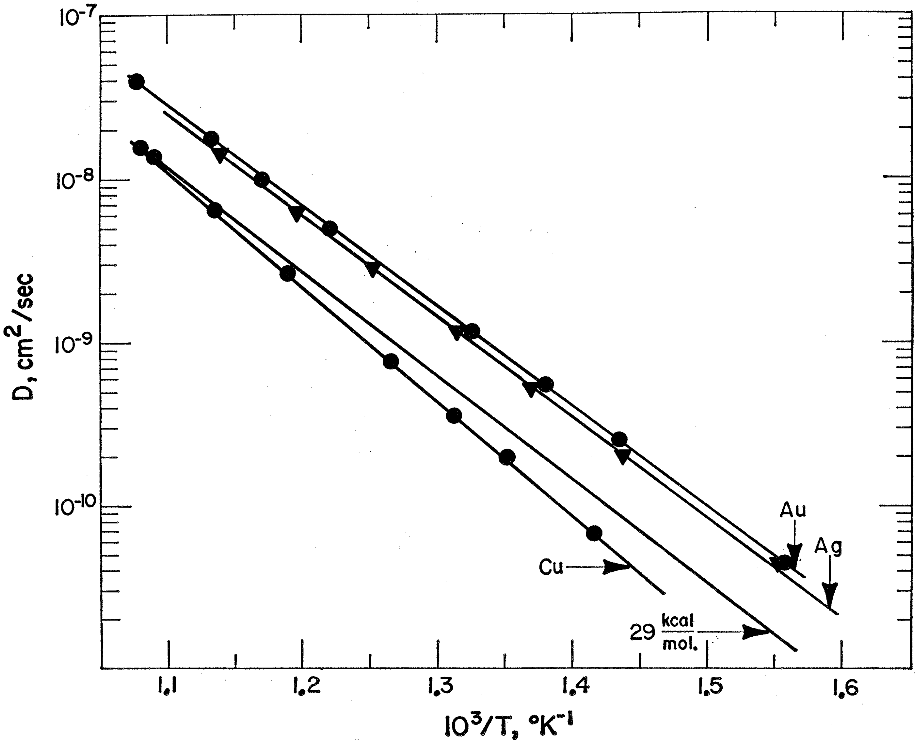

FIG. 3. $\log_{10} D$ versus reciprocal absolute temperature for copper, silver, and gold diffusion in aluminum. The 29-kcal/mole line is common to both Figs. 2 and 3.

of copper. There is no systematic variation of the activation energy for impurity diffusion with the position of the impurity in the periodic table.

Application of Electrostatic Interaction Theory to Diffusion of Impurities in Aluminum

Since the electrostatic interaction theory calculates $\Delta Q = Q_{\text{impurity}} - Q_{\text{self}}$, we must establish the value of Q_{self} in order to compare our results with the theory. This is not a trivial problem in the case of aluminum, because the tracer measurements give $Q=34$ kcal/mole but the best NMR measurements give 28.8 kcal/mole.

Under the proper experimental conditions, tracer diffusion measurements yield the most accurate values of Q. But these conditions cannot be fulfilled for aluminum: The extremely low specific activity ($\tau_{1/2}=7.4\times10^5$ yr) of the only available radioactive isotope of aluminum and the tenacious oxide film which forms on aluminum in air at room temperature make the measurement of self-diffusion in aluminum a difficult experimental problem. Lundy and Murdock[16] attempted to overcome the specific activity problem by not using the thin layer geometry, but by pressure bonding a 0.015-cm–thick disk containing the ^{26}Al to the nonactive sample. Their penetration plots showed a holdup of the tracer at the bond interface, presumably due to an Al_2O_3 barrier, for diffusion anneals below 600°C. Such a holdup changes the boundary condition from an instantaneous source to a continuous source of tracer and may lead to an apparent D that is lower than the true D. Since this effect becomes more pronounced with decreasing temperature, the activation energy deduced from these data (34 kcal/mole) is probably larger than the true value. However, the absolute values of D obtained at high temperature by this technique are probably quite accurate.[17]

Contrary to tracer measurements, NMR measurements may have an uncertainty of as much as a factor of 2 in the absolute value of D and, hence, D_0, but give an accurate value of Q.[18] The most accurate NMR measurement of self-diffusion in aluminum appears to be the work of Fradin and Rowland,[18] who measured D over five decades using the Slichter-Ailion technique.[19,20] We have combined their value of Q(28.8±0.8 kcal/mole) with Lundy's and Murdock's highest temperature value of D (1.29×10^{-8} cm²/sec at 643°C which is an average of two measurements at that temperature) to get

$$D=0.11e^{-29\,000/RT}\ \text{cm}^2/\text{sec} \tag{2}$$

as the best expression for self-diffusion in aluminum.

This equation is shown in Figs. 2 and 3 as the line marked "29 kcal/mole." It suggests that the value of D at the lowest temperature used by Lundy and Murdock is low by a factor of 1.9 owing to holdup of the ^{26}Al tracer by the Al_2O_3 layer at the tracer-sample boundary. This is not unreasonable, as will be shown later.

TABLE I. Tracer diffusion in aluminum.

Tracer	Temp. (°C)	D (cm²/sec)
^{71}Ge	653.2	7.41×10^{-8}
	616.7	3.58×10^{-8}
	576.0	1.58×10^{-8}
	543.8	8.60×10^{-9}
	515.3	4.20×10^{-9}
	485.5	2.14×10^{-9}
	462.5	1.17×10^{-9}
	431.2	5.05×10^{-10}
	401.0	1.92×10^{-10}
^{72}Ga	652.3	5.63×10^{-8}
	614.0	2.98×10^{-8}
	573.0	1.28×10^{-8}
	543.0	6.65×10^{-9}
	512.9	3.43×10^{-9}
	483.0	1.62×10^{-9}
	454.4	7.30×10^{-10}
	429.5	3.50×10^{-10}
	406.7	1.80×10^{-10}
^{65}Zn	652.9	4.04×10^{-8}
	612.8	1.88×10^{-8}
	594.1	1.40×10^{-8}
	578.6	1.01×10^{-8}
	572.0	8.79×10^{-9}
	567.4	8.21×10^{-9}
	542.5	4.89×10^{-9}
	504.1	2.03×10^{-9}
	466.1	7.05×10^{-10}
	452.8	5.04×10^{-10}
^{65}Zn	450.3	5.27×10^{-10}
	409.7	1.41×10^{-10}
	407.3	1.32×10^{-10}
	406.0	1.37×10^{-10}
	366.3	3.50×10^{-11}
	357.0	2.66×10^{-11}
^{64}Cu	651.8	1.56×10^{-8}
	644.8	1.39×10^{-8}
	609.6	6.45×10^{-9}
	572.2	2.70×10^{-9}
	516.4	7.66×10^{-10}
	489.1	3.45×10^{-10}
	467.0	1.97×10^{-10}
	433.0	6.66×10^{-11}
^{110}Ag	655.0	$4.14\times10^{\mathrm{a}-8}$
	648.3	$3.37\times10^{\mathrm{a}-8}$
	604.5	1.41×10^{-8}
	563.8	6.11×10^{-9}
	525.1	2.87×10^{-9}
	487.0	1.18×10^{-9}
	457.1	5.23×10^{-10}
	422.7	2.12×10^{-10}
	371.0	4.38×10^{-11}
^{198}Au	654.6	3.92×10^{-8}
	610.2	1.81×10^{-8}
	582.2	9.77×10^{-9}
	547.1	4.80×10^{-9}
^{198}Au	481.4	1.14×10^{-9}
	450.6	5.60×10^{-10}
	423.5	2.55×10^{-10}
	368.7	4.47×10^{-11}
Tracer	Temp. (°C)	D (cm²/sec)

[a] These two values of D lie significantly above the Arrhenius line of Fig. 3. They were, therefore, not included in the least squares, nor shown on Fig. 3.

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[16] T. S. Lundy and J. F. Murdock, J. Appl. Phys. **33**, 1671 (1962).

[17] The same comments concerning activity holdup apply to the measurements of M. Beyeler and Y. Adda [J. Phys. (Paris) 29, 345 (1968)] who dried a solution of ^{26}Al on the surface of their samples.

[18] F. Y. Fradin and T. J. Rowland, Appl. Phys. Letters **11**, 207 (1967); (private communication).

[19] C. P. Slichter and D. C. Ailion, Phys. Rev. **135**, A1099 (1964).

[20] D. C. Ailion and C. P. Slichter, Phys. Rev. **137**, A235 (1965).

TABLE II. Parameters for impurity diffusion in aluminum.

Tracer	D_0 (cm^2/sec)	Q (cal/mole)
^{71}Ge	0.481	28 980±210
^{72}Ga	0.490	29 240±141
^{65}Zn	0.259	28 860±134
^{64}Cu	0.647	32 270±270
^{110}Ag	0.118	27 830±142
^{198}Au	0.131	27 790±240

Further evidence for $Q=29$ kcal/mole comes from the work of Volin and Balluffi,[21] who measured self-diffusion in aluminum in the 10^{-15}–10^{-19}-cm^2/sec range by following the annealing kinetics of voids by means of transmission electron microscopy. Their values of D disagree radically with an extrapolation of Lundy's and Murdock's data, but agree with Eq. (2) within their limits of experimental error.

In arriving at Eq. (2), we have used what we believe to be the best features of two different types of experiments covering different ranges in temperature. If divacancy contributions are large at 643°C, then Eq. (2) is unreliable. However, the Arrhenius plots in Figs. 2 and 3 are linear over a temperature range that overlaps the ranges of both the tracer and NMR measurements; thus, major divacancy contributions to diffusion in aluminum are unlikely. (The deviations of the 16 individual points for the impurity zinc from the least-squares line are randomly distributed between plus and minus over the temperature range 357–653°C.) We shall analyze the impurity diffusion data making the possibly controversial assumption that Eq. (2) is correct.

The difference in the activation energies between impurity and self-diffusion ΔQ may be expressed as[2]

$$\Delta Q \equiv Q_{\rm imp} - Q_{\rm self} = \Delta E + \Delta H_2 - C, \tag{3}$$

where ΔE is the difference between the energy to form a vacancy next to an impurity atom and the energy to form a vacancy in the pure solvent, and $-\Delta E$ is the impurity-vacancy binding energy. ΔH_2 is the difference between the energy for a vacancy-impurity atom exchange and the energy for a vacancy-solvent atom exchange in the pure solvent. C is the temperature dependence of the correlation factor for impurity diffusion f_i, as given by the expression

$$C = R\frac{\partial \ln f_i}{\partial(1/T)}, \tag{4}$$

where

$$f_i = (w_1 + \tfrac{7}{2}Fw_3)/(w_1 + w_2 + \tfrac{7}{2}Fw_3) \tag{5}$$

and the w_i and F have their usual meaning.[22]

Expressions for ΔE, ΔH_2, and C are obtained from the electrostatic-potential model in terms of the charge on a vacancy $Z_v e$ and the potential $V(r)$ arising from the screened point charge Ze on the impurity ion. The expressions for ΔE and ΔH_2 are

$$\Delta E = Z_v eV(r=a), \tag{6}$$

where V is evaluated at the nearest-neighbor distance a, and

$$\Delta H_2 = Z_v eV(r=\tfrac{11}{16}a) - \Delta E, \tag{7}$$

where V is evaluated at $\frac{11}{16}$ which is the distance between the impurity and the centroids of the half-vacancy hemispheres that flank the impurity at the saddle point. Values of C require the evaluation of ΔH_1, ΔH_3, and ΔH_4 in a manner similar to that for ΔH_2.[2] We have taken $Z_v=-3$, the screening constant $q=2.04$ Å^{-1}, and the Fermi wave vector $k_F=0.922$ a.u., and have used both the Thomas-Fermi and oscillating potentials to calculate $\Delta Q_{\rm th}$ for the diffusion of heterovalent impurities in aluminum.

The values of $\Delta Q_{\rm th}$ thus obtained are very different from $\Delta Q_{\rm exp}$ (Table III). The latter are small; if Eq. (2) is correct, $\Delta Q_{\rm exp}$ for the impurities zinc, gallium, germanium, and antimony is zero. $\Delta Q_{\rm th}$, on the other hand, is very large for $Z<0$. It is smaller for $Z>0$ only because the large value of C partially cancels the large value of ΔH_2. The oscillating potential gives only slightly better agreement between $\Delta Q_{\rm th}$ and $\Delta Q_{\rm exp}$ than the Thomas-Fermi potential. A number of different oscillating potentials[23] also give $\Delta E<1$ kcal/mole for $Z=1$, and yield large values of ΔH_2 similar to those in Table III. It is the large values of ΔH_2 that lead to the large values of C for $Z>0$.

The large values of ΔH_2 are probably the most suspect quantities in Table III because the oscillating potentials used in the calculation are based on weak-perturbation theory, whereas strong perturbations may be expected at the saddle point. Also, phase shifts in the oscillating potentials have been neglected; however, their inclusion in the calculation is not likely to reduce ΔH_2 enough to provide agreement between $\Delta Q_{\rm th}$ and $\Delta Q_{\rm exp}$.

The near-zero and equal values of $\Delta Q_{\rm exp}$ for the diffusion of zinc, gallium, and germanium in aluminum cannot be explained by the LeClaire modification of the electrostatic theory using any reasonable form of the potential, because ΔE and ΔH_2 are of different sign for $Z>0$ and for $Z<0$. If the oscillating potential had an extreme dip at $r=a$, so that ΔE and ΔH_2 were large and of opposite sign, C would still be large for $Z>0$ and near zero for $Z<0$.

The disagreement between $\Delta Q_{\rm th}$ and $\Delta Q_{\rm exp}$ can be reduced by evaluating $V(r)$ in Eq. (7) at $r=14a/16$ instead of $11a/16$. This seems to us to be a rather *ad hoc* modification, notwithstanding Edelglass and

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[21] T. E. Volin and R. W. Balluffi, Phys. Status Solidi **25**, 163 (1968).

[22] J. R. Manning, Phys. Rev. **128**, 2169 (1962).

[23] See, for example, A. Blandin and J. L. Déplanté, in *Size Effects and Chemical Interactions in Metallic Solid Solutions*, edited by J. Friedel and A. Guinier (W. A. Benjamin, Inc., New York, 1963).

TABLE III. Comparison of theoretical and experimental values of ΔQ[a].

Impurity	Potential	ΔE	ΔH_2	C[b]	ΔQ_{theor}	ΔQ_{expt}
Cu ($Z=-2$)	Thomas-Fermi	+2.10	+16.12	0.00	+18.22	+3.2
Ag ($Z=-2$)	Oscillating	−0.30	+9.88	0.00	+9.58	−1.2
Au ($Z=-2$)						−1.2
Zn ($Z=-1$)	Thomas-Fermi	+1.05	+8.06	+0.03	+9.08	−.01
	Oscillating	−0.15	+4.94	+0.10	+4.69	
Ge ($Z=+1$)	Thomas-Fermi	−1.05	−8.06	−7.41	−1.70	−0.0
	Oscillating	+0.15	−4.94	−4.27	−0.52	
Sb ($Z=+2$)	Thomas-Fermi	−2.10	−16.12	−13.40	−4.82	~0.0[c]
	Oscillating	+0.30	−9.88	−7.10	−2.48	

[a] All energies in units of kcal/mole.
[b] For $RT=1.6$.
[c] Data of Ref. 15.

Ohring's arguments.[24] If one calculates ΔH_2 from the changes in the appropriate elastic constants due to the impurity, as Lazarus did in his original paper,[1] one obtains $\Delta H_2=0.02\times\Delta E$. Thus, Lazarus's modification of the electrostatic theory gives good agreement between ΔQ_{th} and ΔQ_{exp}. Although the neglect of the C term is not generally valid, it is likely that C is small since ΔH_2 is small in the Lazarus theory.

The effect of the size of the impurity atom on the activation energy for impurity diffusion may be evaluated from the theory of Swalin.[25] This theory, which is based on the elastic strain around an impurity atom, predicts that all the impurities studied in this investigation should diffuse in aluminum with a larger activation energy than that for self-diffusion. The predicted ΔQ's in kcal/mole are: 1.2 for gallium; 3.5 for copper, zinc, and germanium; 4.9 for silver; and 5.7 for gold. Both the absolute values and the relative values of ΔQ for the various impurities are predicted incorrectly by this theory. However, there is a correlation between the relative values of the solute-diffusion coefficients and the effect of the solutes on the lattice parameter. The addition of 1 at.% of the solutes to aluminum expands the lattice parameter by 0.05% for gallium and germanium, contracts the lattice by 0.02% for zinc, and contracts the lattice by 0.07% for copper. Silver produces no change.[26] Thus, the fastest diffusing impurity (germanium) appears to be the largest, and the slowest diffusing impurity (copper) appears to be the smallest when dissolved in aluminum.

Impurity-Vacancy Binding Energies in Aluminum

We deduce that the impurity-vacancy binding energies in aluminum are small as follows. Equation (3) and the relation between C and the ΔH_i in Ref. 2 should be valid independent of the model used to evaluate ΔE and the ΔH_i. Without a model to suggest the relative magnitudes of ΔE and the ΔH_i, there are a number of values of ΔE, ΔH_2, and C that will give a ΔQ near zero. However, preliminary measurements of the temperature dependence of the isotope effect for zinc diffusion in aluminum give a small value of C (<0.1 eV) and $f_{\text{Zn}}\sim0.65$ (taking $\Delta K=0.9$). Thus, we are left with two alternatives for zinc diffusion in aluminum, (1) ΔH_2 is large and positive and ΔE is equal in magnitude and of opposite sign or (2) both ΔE and ΔH_2 are small. (A large negative value of ΔH_2 is inconsistent with a small value of C.) We believe that near-zero values of ΔE and ΔH_2 are a better explanation of the zinc results because the perturbation introduced by an impurity atom should be much larger when the impurity is in the compressed-saddle-point configuration than when the impurity is located on a lattice site next to a vacancy. Further measurements of the temperature dependence of the isotope effect for zinc and similar measurements for an electropositive impurity like germanium in aluminum would aid in establishing the magnitude of ΔE, ΔH_2, and C. The near-zero values of ΔQ_{exp} for gold, silver, copper, zinc, gallium, germanium, cadmium, and antimony suggest that the impurity-vacancy binding energy is small for all these impurities in aluminum.

Small impurity-vacancy binding energies in aluminum have also been suggested by high-temperature equilibrium measurements. Beaman *et al.*[5] studied dilute Al-Ag and Al-Mg alloys by measuring the excess macroscopic thermal expansion and x-ray lattice parameter change of the alloy relative to pure aluminum on heating; they found a binding free energy of ≤0.01 eV for magnesium and about 0.08 eV for silver. Thus, equilibrium and near-equilibrium techniques give small binding energies; these are also supported by theoretical calculations.[6]

On the other hand, measurements on quenched alloys containing 0.1–5 at.% impurity give much larger binding energies; representative values, taken from

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[24] S. M. Edelglass and M. Ohring, Trans. AIME **245**, 186 (1969).

[25] R. A. Swalin, Acta Met. **5**, 443 (1957).

[26] W. B. Pearson, *Handbook of Lattice Spacings and Structures of Metals and Alloys* (Pergamon Publishing Corp., New York, 1967), Vol. 2, p. 548 ff.

TABLE IV. Impurity-vacancy binding energies in aluminum as determined from quenching and aging studies.[a]

Impurity	Binding energy eV	(kcal/mole)
Mg	0.20	(4.6)
Si	0.26	(6.0)
Cu	0.20	(4.6)
Zn	0.18	(4.1)
Ge	0.28	(6.4)
Ag	0.25	(5.7)
Cd	0.32	(7.4)
Au	0.38	(8.8)
In	0.39	(9.0)
Sn	0.42	(9.7)

[a] Values taken from articles by Doyama (Ref. 4) and Hasiguti (Ref. 27). Binding energy and binding free energy are often used interchangeably in the literature. Most of the tabulated values are binding-free energies.

the review papers of Hasiguti[27] and Doyama,[4] are given in Table IV. The binding energies obtained from quenching studies may vary by a factor of 2 or more from investigator to investigator (see Refs. 28 and 29 and the discussion following them).

It is possible to reconcile the low binding free energies obtained by Beaman *et al.*[5] and the high binding free energies obtained from quenching studies by assuming a very large vibrational entropy of binding, about $3.5k$, and a large enthalpy of binding. (This is because the quenching experiments measure the binding free energy at a much lower temperature than the equilibrium experiments do.) However, this is hard to reconcile with our small values of ΔQ. Specifically, the quenching studies indicate that the binding free energy for gold is 0.15 eV greater than for silver, whereas the activation energies for diffusion, and, hence, by implication the binding enthalpies, are the same for these two elements. The difference in binding entropy between silver and gold must be 3–$4k$ to reconcile the quenching results with the activation energies for diffusion; this, however, would make a difference of at least a factor of 10 in the D_0 values, which differ only by 10%. Hence, we conclude that the entropy of binding cannot explain the difference between the results of high-temperature equilibrium studies and quenching studies.

In our opinion, this difference is due to the fact that the quenching studies do not measure a true impurity-vacancy binding energy. The deduction of a binding energy from quenching studies is based on the assumptions that the impurity atoms are present as isolated atoms after the quench, and that the electrical resistivity per vacancy or per impurity atom is the same whether the defect is associated or free.

The first assumption seems highly unlikely since all of the impurities listed in Table IV are known to cluster (form *G-P* zones) in aluminum. Thus, appreciable impurity-impurity binding must exist in these alloys. The subject has been discussed by Perry,[30] who has shown that the results of Takamura[29] on quenched dilute Al-Zn alloys (up to 0.42 at.% zinc) cannot be accounted for by a single impurity-vacancy binding energy. An impurity-impurity binding energy with a minimum value of 0.1 eV is needed to fit the results. Thus, four binding energies must be considered in the analysis: (1) impurity-vacancy, (2) impurity-impurity, (3) impurity pair-vacancy with the vacancy bound to only one impurity, and (4) the same as (3) but with the vacancy bound to both impurities. If reasonable values are used for 2–4, the data can be fitted with a range of values of the impurity-vacancy binding energy, including zero.

Impurity-impurity binding and clustering can also explain the correlation between apparent vacancy-impurity binding energy and the solubility of the impurity in aluminum. Doyama[4] has pointed out that the smaller the solubility, the higher the apparent binding energy; this is what one might expect from the present argument because the lower the solubility, the larger the tendency for clustering before and during the quench. Doyama has also calculated that the critical temperature at which the defect configuration is frozen during the quench is in the range 50–150°C, depending on quench rate and binding energy. However, for most of the impurities under consideration, the solubility at temperatures significantly higher than the critical temperature is less than the concentration of impurity in the sample. Thus, clustering of impurities during the quench should be expected. We note that the clustering of silver in aluminum at high temperatures has been proposed by Heumann and Böhmer[12] to explain the difference between their data on tracer diffusion and the data on chemical diffusion[31] in the Al-Ag system.

We conclude this section by suggesting that impurity-vacancy binding energies obtained from quenching studies are less reliable than those obtained from high-temperature equilibrium techniques. The former are affected by impurity-impurity binding and by clustering; these give rise to an apparent binding energy that can be much higher than the true impurity-vacancy binding energy.

Diffusion of Transition Metals in Aluminum

We remarked earlier that nontransition-metal tracers all appear to diffuse in aluminum with an activation energy of ~29 kcal/mole. The transition-metal manganese falls into the same class, with $Q=28.8$ kcal/

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[27] R. R. Hasiguti, *Lattice Defects and Their Interactions* (Gordon and Breach, Science Publishers, Inc., New York, 1967), p. 201.

[28] T. Federighi, in *Lattice Defects in Quenched Metals*, edited by R. M. J. Cotterill, M. Doyama, J. J. Jackson, and M. Meshii (Academic Press Inc., New York, 1965), p. 217.

[29] J. Takamura in Ref. 28, p. 521.

[30] A. J. Perry, Acta Met. **14**, 719 (1966).

[31] T. Heumann and S. Dittrich, Z. Elektrochem. **61**, 1138 (1957).

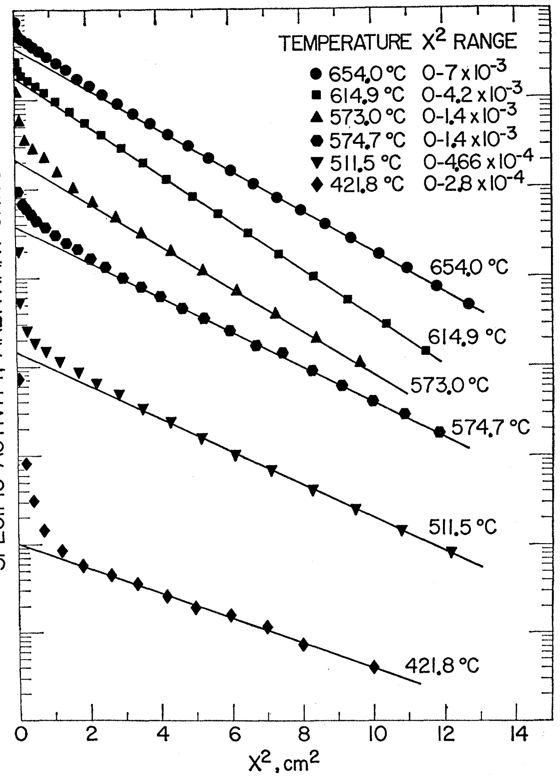

FIG. 4. Log specific activity versus penetration-distance squared for ^{60}Co diffusion in aluminum. The X^2 range indicated in the legend is the value of the range 0–14 on the abscissa.

TABLE V. ^{60}Co diffusion in aluminum.

Temp. (°C)	Time (sec)	D (cm²/sec)
654.0	3.37×10^3	6.9×10^{-8}
614.9	4.37×10^3	2.7×10^{-8}
574.7	1.05×10^4	7.4×10^{-9}
573.0	7.00×10^3	7.0×10^{-9}
551.4	7.84×10^3	4.0×10^{-9}
545.5	7.09×10^3	3.5×10^{-9}
511.5	2.67×10^4	9.8×10^{-10}
482.0	6.83×10^4	4.0×10^{-10}
444.1	2.62×10^5	9.0×10^{-11}
421.8	4.36×10^5	3.5×10^{-11}

mole.[32] However, this correlation stops at manganese. The diffusion of iron in aluminum is described by a high Q and D_0,[11,33] whereas very low values of D_0 and Q are reported for the diffusion of vanadium,[9] chromium,[9] iron,[7] cobalt,[7] nickel,[7] and palladium[8] in aluminum. The latter values do not appear to be representative of volume diffusion and will be discussed in the following section. The two sets of D values for the diffusion of iron in aluminum appear to be representative of volume diffusion and agree within 20% although the values of Q (46 kcal/mole[11] and 63.7 kcal/mole[33]) and D_0 (135[11] and 1.7×10^5 cm²/sec[33]) are rather different. It seems quite clear that D for iron diffusion in aluminum is one to two orders of magnitude lower than for self-diffusion, and that Q for iron is much larger than for nontransition elements.

In an attempt to get more data on the diffusion of transition elements in aluminum, we have measured the diffusion of ^{60}Co in aluminum using evaporated thin layers of tracer and the sectioning techniques described above. The penetration plots (Fig. 4) are curved. They all show a steep slope near $X=0$, followed by a straight line for a factor of 10 or more drop in specific activity. The magnitude of the effect near $X=0$ increases with decreasing temperature. From the straight-line portions of the penetration plots, we obtain the values of D in Table V, and $D=464\exp(-41,740\pm410/RT)$. The penetration plots raise two questions: First, why the steep slope near $X=0$, and second, is the straight-line portion representative of volume diffusion?

The steep slope at small penetrations is not the "near-surface effect" as observed by Mortlock[34] for the diffusion of ^{60}Co in gold, or by Styris and Tomizuka[35] for the diffusion of ^{65}Zn in Cu; the steep slopes extend for hundreds of microns in the present investigation. Nor are the steep slopes due to a small solubility, as suggested by Hirano *et al.*[7] The similarity of the curves for the 573.0°C run (about $\frac{1}{10}$ atomic layer of tracer) and the 574.7°C run (about 10 atom layers of tracer) shows that a change of a factor of 10^2 in the amount of tracer does not change the features of the penetration plots. The present results are very similar to those of Lundy and Padgett[36] on the diffusion of ^{60}Co in silver. They observed similar penetration plots, as well as the fact that lowering the amount of tracer by a factor of 10^4 had only a small effect on the shape of the curves. (We did not look for the time dependence of the shape of the penetration plot reported by them.) The explanation proposed by Lundy and Padgett, that cobalt atoms are preferentially absorbed on the sample surface and, thus, give rise to a curved penetration plot has been questioned by Swisher[37] on thermodynamic grounds. An alternate suggestion that is likely for diffusion in aluminum is that the ^{60}Co diffuses slowly through a thin oxide layer at the tracer-metal interface and then diffuses more rapidly through the metal.[38]

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[32] The measurements on manganese (Ref. 16) were made simultaneously with the aluminum self-diffusion measurements discussed in the section on comparison with the literature. A holdup was again encountered, but it appeared to be temperature-independent. Thus, the value of Q reported is probably right, but the reported D_0, 0.22 cm² sec, is probably low.

[33] G. M. Hood, Bull. Am. Phys. Soc. **13**, 487 (1968).

[34] A. J. Mortlock, Trans. AIME **242**, 1963 (1968).

[35] D. L. Styris and C. T. Tomizuka, J. Appl. Phys. **23**, 1001 (1963).

[36] T. S. Lundy and R. A. Padgett, Trans. AIME **242**, 1897 (1968).

[37] J. H. Swisher, Trans. AIME **245**, 1121 (1969).

[38] In broader terms, we believe the dissolution of the tracer into the base metal may be the limiting step. The slow dissolution may arise from slow diffusion through an oxide layer, slow kinetics of dissolution of the tracer from a compound, etc.

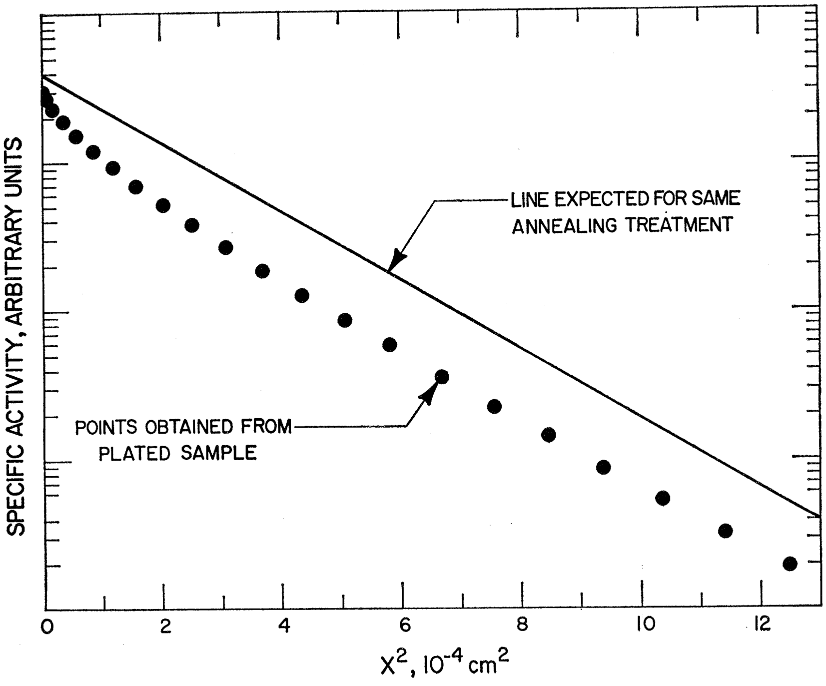

FIG. 5. Log specific activity versus penetration-distance squared for ^{65}Zn diffusion from an electroplated layer into aluminum. The line expected for diffusion from an evaporated layer of tracer for the same annealing treatment is also shown.

This hypothesis allows us to solve the diffusion equation and obtain an answer to the second question posed above. The initial and boundary conditions are no longer an instantaneous plane source at $X=0$, $t=0$ that leads to Eq. (1), but are a continuous plane source at $X=0$, $t>0$. The solution of the diffusion equation for these conditions, assuming a constant source strength, is the sum of an exponential and an error function.[39] This solution fits the penetration plots of Fig. 4 with the same value of D as deduced from the straight lines of Fig. 4 and Eq. (1). Thus, the values of D in Table V may be correct, although the source strength probably varies with time.

That such penetration plots can be obtained under the condition of slow diffusion through an oxide layer can be shown by measuring the diffusion of a non-transition-metal impurity in the presence of an oxide layer on the surface. Since electroplating onto aluminum in an aqueous solution may very well increase the thickness of the oxide layer, we have measured the diffusion of ^{65}Zn into aluminum from a plated layer. The penetration plot is shown in Fig. 5, together with a Gaussian penetration plot constructed for diffusion at the same temperature (467.7°C) and the same time (6.25×10^4 sec) using the data of Table I. A straight line parallel to the Gaussian penetration plot can be drawn through the points at deeper penetration in the former. Thus, our values for the diffusion of cobalt in aluminum appear to be representative of volume diffusion.

In addition to cobalt, we have also made three measurements of the diffusion of ^{51}Cr in aluminum. The penetration plots at all three temperatures were similar to the 614.9°C plot in Fig. 4. The values of D were very low, 8.8×10^{-12} cm^2/sec at 649.4°C (2.49×10^5 sec anneal), 2.2×10^{-12} cm^2/sec at 612.9°C (8.58×10^5 sec anneal), and 7.7×10^{-13} cm^2/sec at 586.0°C (1.91×10^6 sec anneal). These give a Q of about 58 kcal/mole and D_0 of about 5×10^4 cm^2/sec, in good agreement with the results of Fricke.[40] A longer anneal at 651.0°C (7.78×10^5 sec) gave a penetration plot with a less steep slope at small X than at large X, and a lower D (6.5×10^{-12} cm^2/sec) than at 649.4°C. The time dependence indicates that we may not be measuring a true volume-diffusion coefficient.

The interpretation of the diffusion of transition-metal impurities in aluminum is, thus, still an open question. The present data on the diffusion of ^{60}Co and ^{51}Cr in aluminum may not represent true volume diffusion; nevertheless, it is clear that iron, cobalt, and chromium diffuse in aluminum much more slowly than self-diffusion, and with much higher activation energies. These results are in glaring contrast with the low D_0's and Q's reported for some transition metals diffusing in aluminum.

Low Values of D_0 and Q for Impurity Diffusion in Aluminum

Very low values of D_0 and Q for diffusion of vanadium, chromium, iron, cobalt, nickel, palladium, cadmium, indium, and tin in aluminum have been reported by Agarwala and co-workers.[7–9] Several explanations of

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[39] H. S. Carslaw and J. C. Jaeger, *Conduction of Heat in Solids* (Oxford University Press, London, 1959), p. 262.

[40] W. G. Fricke, Jr., in *Aluminum* (American Society of Metals, Metals Park, Ohio, 1967).

these results have been proposed by these authors. In the paper on iron, cobalt, and nickel[7] and chromium,[9] they suggest that diffusion along dislocations, enhanced by the very low solubility of the tracer in the lattice, is responsible for the low values of D_0 and Q.[41] The results for palladium, cadmium, indium, and tin[8] and vanadium[9] are suggested as being representative of true lattice diffusion and defended by an incorrect application of LeClaire's theory.[2] We propose an alternate explanation of the low values of D_0 and Q based on the tracer holdup problem discussed earlier.

The experimental details of Refs. 7–9 that have to be considered in the following discussion are the range in activity and the penetration depth over which the penetration plots were taken, and the condition of the applied tracer layer. In all these studies except the one on vanadium, fairly thick (0.1 μ) tracer layers were deposited by methods that tend to thicken the oxide layer on aluminum. A nitrate solution of cadmium, indium, or tin tracer, or a chloride solution of palladium, was dried onto the surface of the sample.[8] The samples were then heated to convert the tracer nitrate to oxide, or, in the case of palladium, to metal. Since aluminum is chemically much more active than any of these tracer elements, this treatment would oxidize the aluminum. The vanadium tracer was dried on as carrier-free $VOCl_3$,[9] which would also react with aluminum. Iron, cobalt, and nickel[7] and chromium[9] were electroplated onto the sample, a procedure which, as we showed above, can lead to non-Gaussian behavior.

In addition to using questionable deposition techniques, Agarwala and co-workers made measurements over very small drops in specific activity, always less than a factor of 10. Since the above deposition techniques probably give rise to penetration plots similar to those at low temperatures in Fig. 4, the shallowness of the penetrations studied probably limited the measurement to the steeply descending part of the penetration plot and, thus, to a slope that gives a very small D, having no relation to the true D. Thus, the low values of D_0 and Q reported by Agarwala *et al.* probably represent neither volume diffusion nor diffusion along dislocations, but an artifact due to experimental technique. It should be noted that these errors in D are not trivial, but may be more than an order of magnitude.

The preceding comments apply to a lesser extent to the study of self-diffusion in aluminum by Lundy and Murdock.[16] They report an appreciable activity holdup at the sample surface for anneals below 600°C, and, because of the low activity of ^{26}Al, they were not able to carry their penetration plots to the point where surfaces effects may be unimportant. The difference between their lowest temperature value of D and Eq. (2), a factor of 1.9, is about what would be expected from the high-temperature plots of Fig. 4 if only a decade of activity were covered.

It is evident from this discussion that diffusion in aluminum poses an extra experimental problem in the deposition of the tracer. Nevertheless, if care is taken, good reproducibility can be obtained. For example, our results agree well with those of Alexander and Slifkin,[11] even though we evaporated the tracer in vacuum, and they electroplated the tracer, but carried out the anneals in a partial pressure of chlorine gas, which tends to break down the oxide layer. Also, the results of Alexander and Slifkin on the diffusion of iron in aluminum agree with those of Hood,[33] even though Hood deposited his tracer by using a heavy-ion accelerator. We also used this technique on the zinc run at 594.1°C; a Gaussian penetration plot was obtained, and the D was in good agreement with those obtained with an evaporated tracer.

This discussion also makes the point, made before by us,[42] that diffusion samples must be sectioned over at least two, and preferably three decades in specific activity in order to avoid erroneous results due to non-Gaussian behavior near the surface or at deep penetration. In the case of oxide holdups, such as may well occur on aluminum, not sectioning deep enough may lead to order-of-magnitude errors in D.

CONCLUSIONS

(1) The impurities germanium, gallium, zinc, copper, silver, and gold all diffuse in aluminum with an activation energy very close to that of self-diffusion and accurately fit an Arrhenius relation over the temperature range investigated.

(2) There is no systematic variation of the activation energy for impurity diffusion with position of the impurity in the periodic table.

(3) ΔQ calculated from the LeClaire version of the electrostatic interaction theory does not agree with experiment for diffusion in aluminum, whether the Thomas-Fermi or March-Murray potentials are used. The Lazarus version of the theory gives better agreement.

(4) The binding energies of nontransition-metal impurities to vacancies in aluminum are small, less than 0.1 eV.

(5) Cobalt, chromium, and iron diffuse in aluminum much more slowly and with a significantly higher activation energy than nontransition-metal impurities.

(6) Low values of D_0 and Q reported for diffusion in aluminum are probably an experimental artifact.

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[41] This interpretation has been properly critized by R. W. Balluffi, Acta Met. 11, 1109 (1963).

[42] S. J. Rothman, N. L. Peterson, C. M. Walter, and L. J. Nowicki, J. Appl. Phys. 39, 5041 (1968).