Isotope effect for diffusion of zinc and copper in aluminum

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The isotope effect for the diffusion of copper in aluminum is 0.81 ± 0.05 at 656.9° C and 0.89 ± 0.05 at 584.7°C. The isotope effect for the diffusion of zinc in aluminum increases from ~ 0.35 at 415 °C to ~ 0.6 at 654°C with a temperature dependence of 0.1 eV. These results and earlier diffusion data indicate that the impurity-vacancy binding energy is small in aluminum, but they do not resolve the controversy concerning the extent of the divacancy contribution to self-diffusion in aluminum.

I. INTRODUCTION

The initial objective of the present study was to help resolve the controversy regarding the impurity-vacancy binding energy for certain solutes in aluminum. In our earlier studies of impurity diffusion in aluminum,¹ we suggested that the impurity-vacancy binding energy in aluminum is small for gold, silver, copper, zinc, gallium, germanium, cadmium, and antimony. This was not a widely accepted view at the time. Numerous quenching studies on dilute aluminum alloys suggested large impurity-vacancy binding energies,² whereas high-temperature equilibrium measurements³ indicated quite small binding energies. Since that time, additional high-temperature equilibrium measurements⁴⁻⁶ and quenching studies⁷ have yielded small impurity-vacancy binding energies for copper, silicon, silver, magnesium, and zinc in aluminum, in agreement with the position stated in Ref. 1. The values of the isotope effect found in the present research, as well as similar results reported by Bartdorff and Reimers,⁸ further support the conclusions in Ref. 1.

The second objective of our study was to determine the magnitude of the divacancy contribution to self-diffusion in aluminum. Interpretation of the existing results on impurity diffusion does not require a divacancy contribution,^{1,8} but one prevailing interpretation of self-diffusion in aluminum⁹ suggests that divacancies are responsible for more than 50% of the self-diffusion at the melting point. Since diffusion by monovacancies may give rise to a different value of the isotope effect than diffusion by divacancies, a measurement of the isotope effect may help resolve this controversy.

II. EXPERIMENTAL TECHNIQUES

The objective for an isotope-effect experiment is to measure very precisely the relative diffusion of two radioisotopes of the same element in a sample. By the nature of the measurements, an absolute value of the diffusion coefficient of the element is also obtained, but with less precision. The experimental procedures that we used are described in the following paragraphs.

A. Base material

Single crystals were grown from 99.999% pure aluminum by the Bridgman method. Diffusion samples 1 cm in diameter and 1 cm long were spark cut from the single crystals. The ends of the samples were ground flat and parallel and etched lightly. The samples were annealed overnight at 600°C, inspected for defects and monocrystallinity, and re-etched before deposition of the isotope.

B. Isotope deposition

Previous experience has shown that in order to obtain good penetration profiles for diffusion in aluminum, the radioisotopes have to be evaporated in vacuum onto freshly etched single crystals. In case of an isotope-effect experiment, this involves mixing the two radioisotopes in the desired proportions, electroplating them together onto a Pt filament, and evaporating. In the present study, this technique worked well for the ⁶⁷Cu - ⁶⁴Cu mixture, but not for ⁶⁵Zn - ⁶⁹Zn because the Zn deposits were loose, spongy, and difficult to evaporate. $^{68}\mathrm{Zn}$ has a low cross section for neutron capture, $\sim 10^{-25} \text{cm}^2$, so a large mass has to be irradiated to obtain sufficient activity of ⁶⁹Zn. Suitably large amounts of activity were deposited by two techniques. In the first, the ⁶⁵Zn - ⁶⁹Zn ratio was adjusted by mixing appropriate amounts of ⁶⁸Zn and natural Zn in the metallic state, irradiating the mixture, and evaporating it as metal. In the second, ⁶⁸ZnO was irradiated, dissolved, mixed with the appropriate amount of ⁶⁵Zn solution, and electroplated on a filament. The Zn deposit was then scraped into a Pyrex tube containing the aluminum crystals. The

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tube was evacuated, back filled with H_2 , and the Zn was evaporated onto the aluminum by heating the tube with a torch.

C. Diffusion measurements

The diffusion samples were placed in tantalum cups, sealed in quartz ampules under a vacuum of 2×10^{-5} Torr, and annealed in electrical-resistance furnaces for times varying from 1 to 31 h. The annealing temperatures were controlled and measured to better than $\pm 1^{\circ}$ C. The annealing time was corrected for heating and cooling of the specimen.

After the diffusion anneal, the samples were reduced in diameter by trepanning with a spark cutter to eliminate edge effects and then sectioned on a microtome. The slices from each section were collected and weighed on a Mettler micro balance. 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 of the specimen, the density of aluminum, and the weight of the section. The sections were dissolved in boiling concentrated HCl, dried, and redissolved in 1.0-ml dilute HCl. The γ activity of each section was counted in a well-type NaI-Tl scintillation counter. Each section was counted to a minimum of 10⁴ counts above background.

D. Isotope-effect measurements

The isotope effect was determined by the halflife separation technique.^{10,11} The integral activity $A_i(t)$ of each section *i* was counted six or more times in a period approximately five times the half-life of the shorter-lived isotope, and was fit to the time *t* elapsed after an arbitrary zero time by means of

$$A_{i}(t) = A_{\alpha i} \exp(-\lambda_{\alpha} t) + A_{\beta i} \exp(-\lambda_{\beta} t), \qquad (1)$$

where $A_{\alpha i}$ and A_{8i} are the activities at time zero in the *i*th section, and λ_{α} and λ_{β} are the decay constants, of the short-lived (subscript α) and long-lived (subscript β) isotopes, respectively. The decay constants are given in Ref. 10 for ⁶⁴Cu and ⁶⁷Cu and in Ref. 12 for ⁶⁵Zn and ⁶⁹Zn. The sections were counted to 10⁶ impulses each time. Corrections were made for counter dead time and background. The more active sections were diluted to $\sim 5 \times 10^5$ counts/min initial counting rate to keep the dead time correction small; the volume to be counted was maintained constant at 1.0 ml.





III. EXPERIMENTAL RESULTS

A. Diffusion

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

$$\ln c = \text{const.} - x^2/4Dt , \qquad (2)$$

where c is the specific activity of a section, the center of which is a distance x from the original surface, D is the diffusion coefficient, and t is the annealing time. Results from experiments in which the plot of log $c vs x^2$ did not obey Eq. (2) were not used. Typical plots for the diffusion of both zinc and copper in aluminum are shown in Fig. 1. The values of D obtained in these experiments are listed in Table I. The values of D for copper fit well on the Arrhenius plot obtained

TABLE I. Diffusion and isotope effect of $\mathbf{C}\mathbf{u}$ and $\mathbf{Z}\mathbf{n}$ in Al.

Temp (°C)	Time (sec)	D (cm ² /sec)	Ε
Cu			
656.9	3462	1.74×10^{-8}	0.814 ± 0.050
584.7	7 062	3.45×10^{-9}	0.890 ± 0.050
Zn			
654.8	3600	4.83×10^{-8}	0.614 ± 0.014
653.3	3684	4.69×10^{-8}	0.584 ± 0.009
625.7	3414	2.89×10^{-8}	0.508 ± 0.005
567.4	5202	8.21×10 ⁻⁹	0.432 ± 0.019
555.8	14400	6.49×10^{-9}	0.472 ± 0.008
514.1	34 722	2.61×10^{-9}	0.465 ± 0.009
479.2	33 800	1.13×10^{-9}	0.416 ± 0.010
451.0	59640	5.58×10^{-10}	0.396 ± 0.012
450.3	55410	5.30×10^{-10}	0.488 ± 0.020
416.6	110 160	1.93×10^{-10}	0.343 ± 0.007
414.7	64650	1.91×10^{-10}	0.366±0.008

previously.¹ The values of D for zinc range from excellent agreement to as much as 18% above the Arrhenius line of Ref. 1. Treating the present and earlier¹ values of D for zinc in aluminum as members of the same population, we obtain the parameters

 $D_0 = 0.325 \text{ cm}^2/\text{sec}$, $Q = 28150 \pm 160 \text{ cal/mol}$.

The value of Q differs by 2.5% from the earlier value.

The difference between the values of D obtained from ordinary diffusion experiments and isotopeeffect experiments may be due to the larger concentration of zinc in the latter; as stated above, relatively large amounts of zinc had to be deposited to obtain sufficient ⁶⁹Zn activity for the required counting statistics. The concentration of zinc in the first section varied between 0.02 and 0.2 at.% in the isotope-effect experiments; this corresponds to 0.2-2 at. % in the first section near the beginning of the anneal, i.e., a finite chemical gradient. The zinc concentration was at least three orders of magnitude lower in the experiments of Ref. 1. However, no systematic correlation appears to exist between the zinc concentration and the deviation from the Arrhenius line; therefore, we are not convinced that the high zinc concentration is the primary cause of the high values of D obtained from some of the isotopeeffect experiments.

B. Isotope effect

If Eq. (2) is written for the simultaneous diffusion of isotopes α and β , one obtains¹³

$$\ln\left(\frac{c_{\alpha i}}{c_{\beta i}}\right) = \ln\left(\frac{A_{\alpha i}}{A_{\beta i}}\right) = \text{const.} - \ln c_{\alpha i} \left[\left(\frac{D_{\alpha}}{D_{\beta}}\right) - 1\right],$$
(3)

where $c_{\alpha i}$ and $c_{\beta i}$ are the specific activities of the isotopes α and β of isotopic mass m_{α} and m_{β} , respectively, in the *i*th section. The value of the isotope effect for diffusion mechanisms where only one atom changes lattice sites during the jump process is

$$E = \left(\frac{D_{\alpha}}{D_{\beta}} - 1\right) / \left[\left(\frac{m_{\beta}}{m_{\alpha}}\right)^{1/2} - 1\right] = f_{\alpha} \Delta K_{i} \quad . \tag{4}$$

Here f_{α} is the correlation factor for the diffusion of isotope α , and ΔK_i , the correction term for many-body interactions, is the fraction of the kinetic energy at the saddle point, which is associated with motion in the direction of the diffusional jump, that belongs to the diffusing atom. Thus, an accurate measurement of A as a function of time for a number of sections from a diffusion sample will give a value of E [from Eqs. (1), (3), and (4)], the accuracy of which is primarily determined by the accuracy of the radioactive counting procedure.

Plots of $\ln(c_{\alpha}/c_{\beta})$ vs $\ln c_{\alpha}$ are shown for copper in Fig. 2 and for zinc in Fig. 3. The straight-line relationship predicted by Eq. (3) is obeyed; the scatter in the data is reasonable, and the error bars obtained from the least-squares fit of the counting data to Eq. (1) are compatible with the counting statistics. The values of the isotope effect obtained from the slopes of the lines in Figs. 2 and 3 are given in Table I, and the values for zinc in aluminum are plotted on a log scale versus 1/T in Fig. 4. The scatter in Fig. 4 is somewhat larger than the error bars, indicating the possibility of a small systematic error. The isotope effect for zinc in aluminum can be fitted to an Arrhenius-type relationship with

$$C \equiv k \frac{\partial \ln(f)}{\partial (1/T)} = -0.10 + 0.02 \text{ eV}.$$
(5)

As usual, it is assumed throughout the present paper that ΔK is independent of temperature.

IV. DISCUSSION

In Secs. IV A and IV B, we adopt the view that diffusion in aluminum takes place via single vacancies, with an activation energy $Q_{1v}^{\text{self}} = 1.26 \text{ eV},^1$ and ignore the influence of divacancies. The influence of the divacancy contribution is assessed in Sec. IV C.

A. Correlation effects and $\triangle K$

The relationship between the isotope effect and the correlation factor [Eq. (4)] involves a number of assumptions. Schoen¹⁴ and Tharmalingam and



FIG. 2. $\ln[C (6^{7}Cu)/C (6^{4}Cu)]$ vs $\ln[C (6^{7}Cu)]$ for the diffusion of $6^{4}Cu$ and $6^{7}Cu$ in aluminum. Each division on the ordinate is 0.01. Each division on the abscissa is 0.5. $\ln[C (6^{67}Cu)]$ decreases from left to right.

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FIG. 3. $\ln[C(^{65}Zn)/C(^{69}Zn)]$ vs $\ln[C(^{65}Zn)]$ for the diffusion of ^{65}Zn and ^{69}Zn in aluminum. Each division on the ordinate is 0.01. Each division on the abscissa is 0.5. $\ln[C(^{65}Zn)]$ decreases from left to right.

Lidiard¹⁵ thought that Eq. (4) was valid only when the jump direction was an axis of at least twofold rotational symmetry. Bakker¹⁶ and Mehrer *et al.*¹⁷ have since shown that Eq. (4) is valid under much more general conditions, including self-diffusion and impurity diffusion by single vacancies, by divacancies if divacancy dissociation jumps are not allowed, and diffusion by vacancy-impurity pairs in fcc metals even when the jump axis is not an axis of twofold symmetry.

In the derivation of Eq. (4), it was assumed that changing the mass of the tracer atom affects only the tracer jump frequencies and that all nontracer jump frequencies remain unchanged. However, if ΔK is less than unity, the motion of a given atom involves the motion of several atoms, and the frequencies of nontracer atom jumps may no longer be independent of the tracer mass. Bakker¹⁶ and LeClaire¹⁸ have estimated how this affects the validity of Eq. (4). If one assumes that only host atom jumps in which the initial and final positions of the host atom are nearest neighbors of the tracer are affected by the mass of the tracer, then this effect introduced an error no larger than 0.5% in $f\Delta K$ for diffusion in aluminum.

It was also assumed in the derivation of Eq. (4) that the activation energy for defect migration is independent of isotopic mass; i.e., zero-point energy and quantum effects have been neglected. LeClaire¹³ and Ebisuzaki *et al.*¹⁹ considered this effect and have shown that the correction to Eq. (4) that arises from quantum effects is less than 2% for the experiments considered in the present paper. Thus, we believe that the determination of *E* from Eq. (4) is valid for impurity diffusion in aluminum to well within the experimental error.

For diffusion in a pure cubic metal by monovacancies, all vacancy-atom exchanges occur with frequency w_0 . The presence of an impurity atom will change the jump frequencies of the neighboring solvent atoms. If the effect of the impurity on the solvent jump frequencies is short range, four jump frequencies for the vacancy near an impurity atom will differ from w_0 in the fcc lattice: w_1 , the frequency of exchange of a vacancy neighboring an impurity atom with any of the four solvent atoms that are also neighbors of the impurity; w_2 , the frequency of exchange of the impurity and the vacancy; w_3 , the frequency of exchange of a vacancy neighboring an impurity with any of the seven solvent atoms adjacent to the vacancy but not neighbors of the impurity (dissociation jump); and w_4 , the frequency of the association jump (reverse of a w_3 jump). All other jumps are assumed to occur with the frequency w_0 . For this model, the correlation factor for impurity diffusion by monovacancies in the fcc lattice, f_i , is given by

$$f_i = \frac{w_1 + \frac{7}{2}Fw_3}{w_1 + w_2 + \frac{7}{2}Fw_3},$$
 (6)

where F is a known function of w_4/w_0 .²⁰ Since the temperature dependences of the various w_i 's will,





in general, be different, f_i may vary with temperature but must be in the range $0 < f_i < 1$. For impurities that diffuse more slowly than self-diffusion, w_2 will be less than the solvent jump frequencies and frequently (but not necessarily) $f_0 < f_i < 1$, where f_0 is the correlation factor for self-diffusion ($f_0 = 0.781$ for diffusion by monovacancies in the fcc lattice).

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Since the maximum value of both f_i and ΔK is unity, the value of *E* for copper in aluminum requires ΔK_{Cu} to be in the range $0.9 \le \Delta K_{Cu} \le 1$; i.e., $\Delta K_{Cu} = 0.95 \pm 0.05$. As the masses of the zinc and copper atoms are nearly equal, it is appropriate to assume $\Delta K_{Cu} = \Delta K_{Zn}$ in aluminum.²¹

Resonant vibrational modes associated with an impurity could make ΔK_i for impurity diffusion significantly different from ΔK_0 for self-diffusion. Impurities heavier than the host atoms will give rise to resonant modes that are characterized by a large amplitude of vibration of the impurity atom or of those atoms which interact directly with the impurity. Feit²¹ and Achar²² have developed expressions for ΔK_i relative to ΔK_0 based on the dynamical theory of diffusion. Both theories suggest that $\Delta K_{Cu} = \Delta K_{Zn}$ and that ΔK_{Cu} is within 5% of ΔK_0 (Feit's theory suggests $\Delta K_{Cu} = 1.02 \Delta K_0$). Thus, it is reasonable to assume $\Delta K_0 = 0.95 \pm 0.05$ for self-diffusion in aluminum.

Given the above value of ΔK_{Cu} , the value of f_i for copper in aluminum at the lower temperature

is ~0.95, i.e., quite close to the upper limit of f_i . This strongly suggests that copper atoms diffuse more slowly in aluminum than aluminum atoms. The temperature dependence of E for copper diffusion may be zero, within experimental error. However, the slight decrease of E with an increase in temperature suggested by the data is what one would expect for a slow-diffusing impurity.²³ With an increase in temperature, the effect of impurity-defect interactions will decrease and f_i will approach f_0 for self-diffusion.

The values of f_i for zinc in aluminum increase with an increase in temperature and are less than f_0 as one would expect for a fast-diffusing impurity.²³ It is argued in Sec. IV B that the magnitude of the temperature dependence of f_i is consistent with a small zinc-vacancy binding energy in aluminum.

B. Impurity-vacancy binding energies

The difference in the activation energies between impurity and self-diffusion, ΔQ , may be expressed as²³

$$\Delta Q \equiv Q_{\rm inp} - Q_{\rm self} = \Delta E + \Delta H_2 - C , \qquad (7)$$

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 ($-\Delta E$ 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 [Eq. (5)]. If $Q_{self} = 1.26 \text{ eV}, ^1 \Delta Q$ is nearly zero (0.05 eV or less) for the diffusion of gold, silver, zinc, gallium, germanium, cadmium, and antimony, and 0.14 eV for the diffusion of copper in aluminum.¹ Without a model to suggest the relative magnitudes of ΔE and ΔH_i , a number of sets of values of ΔE , ΔH_2 , and C exist that will give a ΔQ near zero. However, the measured value of C = -0.10 eV for zinc in aluminum allows only two alternatives; (i) ΔH_{α} is large and positive and ΔE is equal in magnitude and of opposite sign, or (ii) 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 the preferred explanation of our results on zinc because (i) $f_{Z_n} < f_0$ suggests $\Delta H_2 < 0$, and (ii) the perturbation introduced by an impurity atom may be expected to be much larger when the impurity atom is in the compressed saddlepoint configuration than when it is located on a lattice site neighboring a vacancy.¹ Calculations based on the electrostatic model of LeClaire²³ suggest that a small negative value of C is consistent with a small (but larger) negative value of ΔH_2 and smaller value of ΔE . Thus, the present isotope-effect results are consistent with the view that the zinc-vacancy binding energy is small in aluminum. The same appears to be true for silver in aluminum, as Bartdorff and Reimers⁸ have recently reported $C = -0.069 \pm 0.008$ eV for that system, which is close to our value for zinc

in aluminum. An analysis²⁴ of Bartdorff and Reimer's results in terms of the thermo-dynamic model of Neumann and Hirschwald²⁵ yields a small binding energy, 0.03 eV, $Q_{self} = 1.36$ eV and a small divacancy contribution, consistent with the present results.

C. Contribution of single and divacancies to diffusion in aluminum

The contribution of divacancies, the curvature of the Arrhenius plot, and the activation energy for self-diffusion in aluminum are still the subject of controversy. The relevant data on diffusion in aluminum are the following. Tracer measurements at high temperatures give Q = 1.48 eV,^{26,27} whereas NMR measurements at lower temperatures give 1.26 eV.^{26,29} Self-diffusion coefficients deduced from the annealing kinetics of voids³⁰ at still lower temperatures support the lower activation energy. Arrhenius plots for impurity diffusion^{1,31,32} are straight within experimental error, with Q values within ± 0.05 of 1.26 eV for most impurities.

1. Interpretation of self-diffusion in aluminum-large divacancy contribution

Seeger *et al.* have combined the tracer^{26,27} and selected NMR measurements²⁹ of self-diffusion, and have obtained good agreement between measured tracer *D*'s and *D*'s calculated from the NMR measurements. They obtain a strongly curved Arrhenius plot and a 50% divacancy contribution to diffusion at the melting point, although neither measurement alone supports a curved Arrhenius plot. They calculate $Q_{1v}^{self} = 1.28 \text{ eV}$ and Q_{2v}^{self} = 1.59 eV. In our opinion, analyses based on curved Arrhenius plots obtained from measurements by different investigators, different techniques, and in different temperature ranges, are suspect.

2. Interpretation of self-diffusion in aluminum-small divacancy contribution

As an alternative explanation, Volin and Balluffi³⁰ and the present authors¹ have suggested that the lower-temperature tracer measurements²⁶ are influenced by hold up of the tracer, presumably by an Al_2O_3 barrier, and should not be used in the analysis; however, the preexponential term D_0 should be consistent with the highest-temperature tracer data where tracer hold up was less evident. An analysis¹ based on the high-temperature tracer measurements,²⁶ the NMR results of Fradin and Rowland,²⁸ and the low-temperature annealing kinetics of voids³⁰ leads to a linear Arrhenius plot over 11 orders of magnitude with no evidence of a divacancy contribution to diffusion.

Additional support for a linear Arrhenius plot for self-diffusion in aluminum is obtained from accurate measurements of tracer-impurity diffusion. The impurity-diffusion coefficients are similar in value to the self-diffusion coefficients, but no curvature is observed in the Arrhenius plots for the diffusion of seven tracers over a temperature range for which the analysis of Seeger *et al.* would suggest noticeable curvature.^{1,31,32} Recent measurements by Hirano and Fujikawa³¹ show that the Arrhenius plot for zinc diffusion in aluminum is linear over seven orders of magnitude in *D*.

The present measurements on copper diffusion in aluminum support the smaller activation energy for self-diffusion. The magnitude of the selfdiffusion coefficient at the melting point is the same for both the low-activation-energy interpretation (Q = 1.26 eV; Ref. 1) and the divacancy interpretation with a higher effective activation energy ($Q_{\text{eff}} = 1.48 \text{ eV}$),⁹ and this magnitude is the same as the copper-diffusion coefficient in alum-

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inum at the melting point. The value of the isotope effect for copper diffusion in aluminum strongly suggests that copper atoms diffuse more slowly than aluminum atoms in aluminum (see above). Hence, the activation energy for copper diffusion in aluminum, Q_{Cu} , must be greater than Q_{self} ; i.e., $Q_{\text{self}} < 1.40 \text{ eV}$,¹ which supports the low-activation-energy interpretation.

3. Contribution of divacancies to impurity diffusion

The treatment of Seeger *et al.* of self-diffusion requires an explanation of why divacancies exchange much more frequently with aluminum atoms than with impurity atoms. A possible answer to this question may be found in the work of Mehrer³³ who has derived the following expression for the correlation factor for impurity diffusion by di-vacancies in the fcc lattice:

$$f_{i_{*}2v} = \frac{w_{3}' F'}{w_{2}' + w_{3}' F'}, \qquad (8)$$

where w'_{2} is the vacancy-impurity exchange frequency when both vacancies of the divacancy are nearest neighbors of the impurity; w'_1 is a solvent-vacancy exchange frequency that reorients the divacancy so that both vacancies are nearest neighbors of the impurity before and after the jump; w'_3 is a solvent-vacancy exchange frequency that separates one of the two vacancies from the impurity (dissociation jump); and F' is a known function of w'_3/w'_1 . All other jump frequencies are assumed to be equal to w'_0 , which is the average solvent-divacancy exchange frequency in the pure solvent. If the impurity is tightly bound to the divacancy, $w'_3 \rightarrow 0$ and $f_{i,2v} \rightarrow 0$. Hence, the impurity-diffusion coefficient by divacancies may be quite small; on the other hand, impurity diffusion by monovacancies remains finite even if no dissociation of the impurity-monovacancy complex is allowed. Thus, if the impurity is tightly bound to the divacancy, impurity diffusion by divacancies may be quite small when self-diffusion by divacancies is rather large.

To test the general philosophy of the above paragraph, we have performed the following simple calculation of D_{imp} and E for zinc diffusion in aluminum based on the monovacancy-divacancy parameters of Seeger *et al.* over the temperature range investigated in both the present paper and Ref. 1. We take

$$D_{\rm imp,1v} = (D_{1v}^{\rm self} / f_{0,1v})(w_2/w_0) f_{i,1v} , \qquad (9)$$

$$D_{imp_{*}2v} = (D_{2v}^{self} / f_{0,2v})(w_{2}'/w_{0}')f_{i,2v}, \qquad (10)$$

$$E = \frac{D_{\text{imp},2\nu}}{D_{\text{imp},1\nu} + D_{\text{imp},2\nu}} (f \Delta K)_{2\nu} + \frac{D_{\text{imp},1\nu}}{D_{\text{imp},1\nu} + D_{\text{imp},2\nu}} (f \Delta K)_{1\nu} .$$
(11)

We calculate D_{1v}^{self} and D_{2v}^{self} from the parameters of Seeger *et al.*; $f_{0,1v}$ and $f_{0,2v}$ are known (0.78 and 0.47, respectively). We assume that the impurityvacancy binding energy is small and the impuritydivacancy binding energy is such that $f_{i,2v} = \frac{1}{3} f_{i,1v}$. We calculate w_2/w_0 from the experimental values of f_i and D_{imp} by the relation

$$D_{\rm imp} / D_{1v}^{\rm self} = (w_2 / w_0) (f_i / f_0) \,. \tag{12}$$

We take $f_{i,1v} = f_i$ (experimental), assume w'_2/w'_0 = w_2/w_0 , and then calculate D_{imp} and E as a function of temperature with assumed values of ΔK_{1v} = $\Delta K_{2v} = 0.95$ to test Mehrer's hypothesis. Although it is clear that the curvature in the Arrhenius plot of D^{self} , over the range investigated, could be detected experimentally, the curvature in D_{imp} is sufficiently small, due to the small assumed value of $f_{i,2v}$, that it would probably go undetected over the temperature range investigated in Ref. 1. The value of E shows a smooth increase with temperature that is similar in shape to the experimental results in Fig. 4, but with a smaller slope.

Thus, it would appear that a large impuritydivacancy binding energy, which results in a small value of $f_{i,2v}$, may explain why linear Arrhenius plots are observed for impurity diffusion when a sizable divacancy contribution is present in self-diffusion. However, it is not clear why a large impurity-divacancy binding energy exists for impurities when the impurity-monovacancy binding energy is small (or possibly negative in the case of copper).

The temperature dependence of the isotope effect for zinc and silver diffusion in aluminum is clearly compatible with a linear Arrhenius plot but does not eliminate a divacancy contribution, as suggested in Ref. 8. That divacancies should not give rise to curved Arrhenius plots for impurity diffusion is also predicted by McKee and Stark.³⁴ They claim that any increase in jump frequency brought about by divacancies is precisely canceled by a corresponding decrease in the correlation factor for diffusion by divacancies, independent of the impurity-divacancy binding energy. However, some errors may exist in this work.³⁵

4. Results from other types of experiments

The conclusion to be drawn from the above arguments is that one cannot choose between the "small divacancy contribution" and "large diva-

and

cancy contribution" theories only on the basis of measurements of diffusion and the isotope effect. However, analysis of recent experiments on defect annealing following quenching from different temperatures^{36,37} supports the presence of divacancies, and yields $H_{1v}^{M} = 0.65 \text{ eV}, H_{2v}^{M} = 0.50 \text{ eV}$, and $H_{2v}^{B} = 0.20 \text{ eV}$. Combining these results with $H_{1v}^{F} = 0.66 \text{ eV}$ from recent positron-annihilation measurements³⁸ gives,

$$Q_{1v}^{\text{self}} = H_{1v}^{M} + H_{1v}^{F} = 1.31 \text{ eV}$$

and

$$Q_{2n}^{\text{self}} = 2H_{1n}^F - H_{2n}^B + H_{2n}^M = 1.62 \text{ eV},$$

in excellent agreement with the values calculated by Seeger *et al.*⁹ some six years earlier. The defect-annealing experiments also indicate that the simultaneous operation of single and divacancies is more likely to be the mechanism of diffusion in aluminum than the single defect with temperature-dependent parameters proposed by Gilder and Lazarus³⁹ or the double-jump mech-

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If we accept the hypothesis that the divacancy contribution to impurity diffusion in aluminum is small but to self-diffusion is large, the conclusion of Sec. IV B that the impurity-single-vacancy binding energy is small remains qualitatively valid, as does the discussion of correlation and ΔK in Sec. IV A.

V. CONCLUSION

The diffusion of impurities in aluminum appears to take place via weakly bound single vacancies, although a large divacancy contribution to selfdiffusion may exist.

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