than our final procedure based on minimizing the free energy. This can be seen in the fact that Ascher finds an orthorhombic group, not allowed by our analysis. Actually, Ascher's procedure is correct when the distortions form a two-dimensional representation, but will permit too many groups for three-dimensional representations. (We conjecture that the latter case will persist for the higher-dimensional representations arising when translational symmetry is lost.) This is because the maxima and minima of the lowest-order polynomials occur at points where symmetry is maximal, but in three dimensions this is also true for saddle points. It is also our opionion that Ascher's method is no simpler than Landau's method, as used in the text.

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Analysis of Self-Diffusion and Quenching Studies in Aluminum and Gold*

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The analysis of available experimental data for self-diffusion in Al and Au shows that the apparent activation energy increases with increasing temperature. It is shown that this behavior cannot be due only to a divacancy contribution to the high-temperature diffusivity, since this contribution would have to be too large. An explanation which is consistent with the results of quenching studies can be formulated in terms of a temperature dependence of the motion enthalpy H_m^{1v} of single vacancies. In Al, H_m^{1v} is found to increase from 0.46 to 0.72 eV between 225 and 650°C, and in Au from 0.71 to 0.83 eV between room temperature and 1025°C. The conclusions of this investigation are especially important for the identification of quenched-in defects and for the study of thermally activated processes in general.

INTRODUCTION

DIFFUSION theory shows that the activation energy Q for self-diffusion by the vacancy mechanism is equal to the sum of the enthalpies of formation H_f^v and migration H_m^v of vacancies: $Q=H_f^v+H_m^v$. This theoretical relation has frequently been used to determine one of the quantities when the other two are known. In equilibrium measurements, for example, one determines H_f^{1v} experimentally and uses a known value of Q to determine the motion enthalpy H_m^{1v} of single vacancies. In quenching studies, one determines the enthalpy of formation of single vacancies H_f^{1v} and the migration enthalpy of the quenched-in defects H_m; if Q is known, and if $H_f^{1v}+H_m=Q$, the quenched-in defects are identified as single vacancies. If, on the other hand, $H_f^{1v}+H_m\neq Q$, this is interpreted as strong evidence that the defects involved cannot be single vacancies.

Frequently, it has been found that $H_f^{1v}+H_m<Q$. For example, in gold, the formation enthalpy of single vacancies H_f^{1v} is generally accepted to be 0.97±0.02 eV while the experimental value for the migration enthalpy of quenched-in defects is 0.71±0.03 eV. The sum of these two values, 1.68 eV, is less than the accepted value of $Q=1.81$ eV. In aluminum, also, one would not identify the quenched-in defects as single vacancies when the data are compared with the theoretical relationship. Here $Q=1.48$ eV and $H_f^{1v}=0.76$ eV yielding $H_m=0.72$ eV, which is higher than all values determined for the motion enthalpy of quenched-in defects.

The fact that $H_f^{1v}+H_m$ is often not equal to Q is usually interpreted by invoking the presence of divacancies in the quenched metal as a result of vacancy association during the quench. An important consequence of this assumption involves the value of the binding energy of the divacancy which is the subject of much discussion. Another way of explaining some of the results is to postulate a temperature dependence in the motion enthalpy of single vacancies.[1] The object of the present paper is to discuss in detail these two concepts and their consequences, based on the critical examination of all the readily available and pertinent information on aluminum and gold.

EXPERIMENTAL DATA

Figures 1 and 2 show the available data for self-diffusion in Al and Au. The data for Al were determined using radioactive tracers at high temperatures[2] and nuclear magnetic resonance (NMR) techniques at low temperatures.[3,4] The lowest temperature data in Al, obtained by observing void shrinkage,[5] is not shown but

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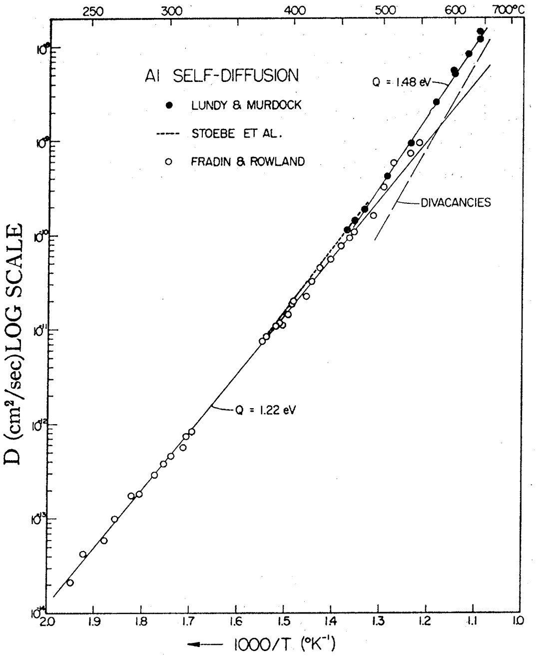

FIG. 1. Self-diffusion data in aluminum. The straight lines shown have been fitted to the extreme low- and high-temperature data. The postulated divacancy contribution is obtained from the difference between the high-temperature diffusivity and the extrapolated low-temperature diffusivity.

agrees well with the continuation of the NMR data to lower temperatures.

The data for Au were determined using radioactive tracer techniques.[6–9] The low-temperature data of Okkerse[6] have been criticized[7] for lack of a proper warmup correction and a possible burring problem. However, the warmup correction has been made by Okkerse[10] and the burring problem, which would lead to consistently high values of D, is probably negligible since these results agree well with others in the region of overlap. Therefore, it is felt that the only reason why Okkerse's results differ from the others is the emphasis on the low-temperature region. Pipe diffusion is unlikely to play a significant role in Okkerse's experiment since for typical dislocation densities in Ag one does not observe[11] this effect above $0.65T_m$, and the effect in Au should be comparable. Nor in Al can the low-temperature diffusion data be influenced by pipe diffusion, because NMR techniques avoid pipe-diffusion problems.

It is apparent from the data that neither in Fig. 1 nor in Fig. 2 can one draw a straight line through all of the points; rather there is a trend of increasing slope in the diffusivity plot with increasing temperature. For simplicity of analysis, it is observed that two straight lines may be drawn through both the Al and Au points by fitting straight lines to the extreme low- and high-temperature data. The resulting lines can be analyzed in terms of the parameters in the diffusion equation $D=D_0 \exp(-Q/kT)$. The resulting values are given in Table I. While the NMR data have been corrected for jump correlations, and the tracer data have not, this in no way affects the results of the following analysis.

DISCUSSION

Divacancies

One may attempt to analyze the total diffusivity D shown above in terms of a divacancy contribution at the high temperatures, $D=D^{1v}+D^{2v}$, where $1v$ and $2v$ refer to single and divancies, respectively. The resulting parameters D_0^{2v} and Q^{2v} for divancy diffusion are shown in Table I, and the corresponding lines are given in the figures.

If the high-temperature diffusivity contains a divacancy contribution, the diffusivity at sufficiently low temperatures must be due to single vacancies alone. In Al, this means that for diffusion via single vacancies the activation energy Q for single vacancy diffusion is about 1.22 eV. Using this value, one can determine the motion enthalpy H_m^{1v} of a single vacancy in Al from 1.22 eV$=H_f^{1v}+H_m^{1v}$. H_f^{1v} has been determined by a number of authors both by quenching and equilibrium studies, over the temperature range 280–650°C. The mean value of 10 determinations[12–20] (three equilibrium and seven quenching) is 0.76 eV with a standard deviation of only 0.014 eV. From this it follows that $H_m^{1v}=0.46$ eV for Al.

This value for the motion enthalpy of single vacancies is not inconsistent with most of the low-temperature annealing studies after quenching.[12,16–21] This is especially true if one interprets the recovery data obtained after low-temperature quenching (below 400°C) as due to single vacancies, the data obtained by quenching from near 470°C as due to divacancies, and the higher-temperature quenching data as being influenced by re-

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arrangements of dislocations caused by quenching strains.

The divacancy contribution to the diffusion process at high temperatures may be analyzed by noting that the activation energy of the divancy contribution is given by[22]

$$Q^{2v}=2H_f^{1v}-H_b^{2v}+H_m^{2v}, \tag{1}$$

where H_b^{2v} is the divacancy binding enthalpy and H_m^{2v} is the motion enthalpy of divacancies. For the case of Al (see Table I), $Q^{2v}=1.8$ eV. This gives $H_m^{2v}-H_b^{2v}=0.28$ eV. For $H_b^{2v}=0.1$ eV one finds $H_m^{2v}=0.38$ eV.

The results of Simmons and Balluffi[23] indicate a monovacancy abundance in Al of more than 90% for a divacancy binding energy of 0.1 eV. If the data in Fig. 1 are to be explained by the presence of divacancies, however, the divacancy contribution must be extremely large. Assuming that the observed high-temperature increase in D over the extrapolation of the low-temperature data is entirely due to divacancies, one obtains $D_{1v}/D_{2v}=0.55$ at the melting point of Al.

The ratio of monovacancy and divacancy tracer diffusivities may be written as[24]

$$\frac{D_{1v}}{D_{2v}}=\frac{3\nu_{1v}}{2\nu_{2v}}\frac{c_{1v}}{c_{2v}}\exp[-(G_m^{1v}-G_m^{2v})/kT], \tag{2}$$

where c is the concentration, $G_m=H_m-TS_m$ is the Gibbs free energy of migration, and ν is a frequency factor. Since it is being assumed for this calculation that the curvature in the diffusivity plots is due to divacancies, the motion energy of single vacancies is taken as 0.46 eV, and the above-derived value of 0.38 eV based on an H_b^{2v} value of 0.1 eV, is used for H_m^{2v}. For the other quantities in Eq. (2), the following reasonable values are used[15]: $\nu_{1v}=2\nu_{2v}$, $S_{1v}^m=2S_{2v}^m=2k$. This gives $c_{1v}/c_{2v}=0.5$ at the melting point of Al, which indicates a monovacancy abundance of only 33%, in contradiction with the Simmons and Balluffi result.[23]

TABLE I. Summary of diffusion data.

	Low T	High T	Divacancies
	Aluminum		
Range of good fit (°C)	225–325	500–650	500–650
Q(eV)	1.22	1.48	1.8
D_0 (cm²/sec)	0.02	1.7	9.0
	Gold		
Range of good fit (°C)	600–750	875–1025	875–1025
Q (eV)	1.72	1.81	2.25
D_0 (cm²/sec)	0.04	0.10	1.2

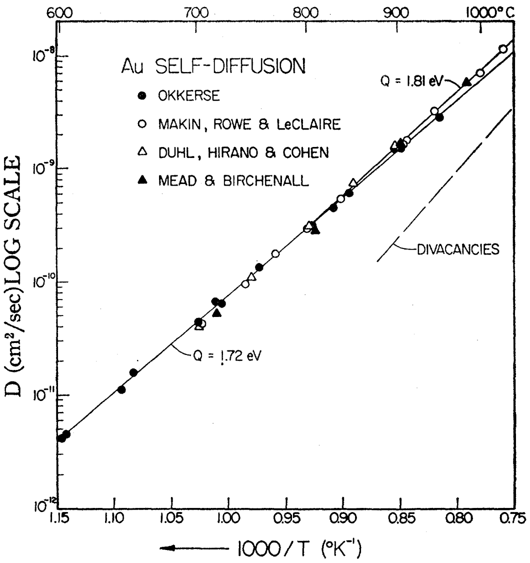

FIG. 2. Self-diffusion data in gold. (See also the caption of Fig. 1.)

This derived value, in turn, may be used to calculate the binding energy of divacancies using the equation

$$c_{2v}=6c_{1v}^2\exp(G_b^{2v}/kT)$$

or

$$c_{1v}/c_{2v}=\tfrac{1}{6}\exp(G_f^{1v}-G_b^{2v})/kT, \tag{3}$$

where G_b^{2v} is the Gibbs free energy of binding of a divacancy, $G_b^{2v}=H_b^{2v}-TS_b^{2v}$. Using Eq. (3) and assuming[15] $S_f^{1v}=2k$, and taking $S_b^{2v}=0$, this yields $H_b^{2v}=0.8$ eV, which further emphasizes the inconsistency of the divacancy model. This high value of H_b^{2v} is a consequence of the high divacancy concentration (low monovacancy abundance) necessary to account for the temperature dependence of D and has a weak dependence on the assumed entropy values.

One can also attempt to analyze the diffusion results in Au in terms of a divacancy contribution at high temperatures. The resulting parameters have been indicated in Table I, and the corresponding line has been shown in Fig. 2. Using an analysis similar to that of the previous case, the activation energy for diffusion via single vacancies must be 1.72 eV in Au. The enthalpy of formation of single vacancies in Au is 0.97 eV with a standard deviation over ten measurements[13,16,25–31] of 0.010 eV in the temperature range 550–1030°C. Using these values, one obtains $H_m^{1v}=0.75$ eV.

This value for the motion enthalpy of single vacancies is closer to the value usually observed for the migration

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energy of quenched-in defects in gold than is the normally assumed value,[32–34] $H_m^{1v}=0.83$ eV. Apparent motion enthalpy values usually observed in quenching experiments[33,34] range from 0.6 to 0.76 eV. The former value is normally observed at high quenched-in vacancy concentrations[33,34] and at the lowest annealing temperatures and might very well be due to a divacancy contribution to the measured enthalpy of motion. The mean of the remaining values is 0.71 eV and is measured at about room temperature.

The analysis of the high-temperature diffusion data in terms of a divacancy contribution in Au using Eq. (1) and $Q^{2v}=2.25$ eV (see Table I) yields $H_m^{2v}-H_b^{2v}=0.29$ eV. This indicates a value for H_b^{2v} of about 0.3 eV if H_m^{2v} is taken as 0.6 eV. These values appear to be reasonable in terms of the annealing data discussed above.

However, by analyzing the data in terms of Eqs. (2) and (3), with $D_1/D_2=3.0$ as observed at the melting point, $H_m^{1v}=0.75$ eV, $H_m^{2v}=0.61$ eV, and assuming[32] $S_f^{1v}=k$ in Au, one obtains $c_1/c_2=1.3$. This indicates a monovacancy abundance of 57% at the melting point and a divacancy binding enthalpy $H_b^{2v}=1.03$ eV.

This divacancy binding enthalpy in Au, as in Al, is much higher than values consistent with experimental results. These values for H_b^{2v} are higher than would be indicated by Simmons and Balluffi's monovacancy abundance plots[24,35] because of the different values of H_m used here as well as the fact that larger vacancy clusters are ignored. However, neither the inclusion of trivacancy considerations, nor the assumption of entropy values differing by a factor of 2 from those used here, would reduce the H_b^{2v} values to reasonable ones. It therefore must be concluded that the increase in slope of the diffusivity plot with increasing temperature in Au and Al cannot be explained solely by the presence of divacancies at the melting temperatures and that one must look for another explanation for this phenomenon.

Temperature Dependence of H_m^{1v} and S_m^{1v}

An alternate explanation for the observed temperature dependence of the diffusion activation energy Q may be formulated in terms of a temperature dependence of the enthalpy and entropy of motion of single vacancies. Theoretically, it has been shown that the temperature dependence of H_f^{1v} and S_f^{1v} is too small to be detected using current experimental methods.[36] Experimentally, it has been shown above that H_f^{1v} is temperature independent within about 1.5%. The observed temperature dependence in Q is several times more than this as has been noted in Table I.

There is no theoretical reason why H_m^{1v} should be temperature-independent. This is especially true for the case where the vacancy jump is not reversible and if one takes anharmonic terms into account.[37] Since the reaction rate model does not show that D_0 and Q are necessarily temperature-independent, and one has only the thermodynamic identity,

$$(\partial H/\partial T)_p=T(\partial S/\partial T)_p,$$

it is impossible to separate a temperature dependence in H_m^{1v} from that in S_m^{1v}.

One can determine an effective activation energy for diffusion by writing

$$D=A\exp(-G/kT), \qquad (4)$$

where G is the Gibbs activation free energy for diffusion. For the case of diffusion via single vacancies alone, one has

$$G=G_f^{1v}+G_m^{1v}. \qquad (5)$$

If G is temperature-dependent, the effective activation energy at any temperature G_{eff} is defined as[38]

$$G_{\mathrm{eff}}=-\frac{\partial \ln D}{\partial(1/kT)}=G-T\frac{\partial G}{\partial T}. \qquad (6)$$

Expressing G as a power expansion around a temperature T_0, one has

$$G=(G)_{T_0}+\left(\frac{\partial G}{\partial T}\right)_{T_0}(T-T_0)+\frac{1}{2}\left(\frac{\partial^2 G}{\partial T^2}\right)_{T_0}(T-T_0)^2+\cdots. \qquad (7)$$

Substituting Eq. (7) into Eq. (6), this yields

$$G_{\mathrm{eff}}=(G)_{T_0}-\left(\frac{\partial G}{\partial T}\right)_{T_0}T_0-\frac{1}{2}\left(\frac{\partial^2 G}{\partial T^2}\right)_{T_0}(T^2-T_0^2). \qquad (8)$$

Since

$$\left(\frac{\partial G}{\partial T}\right)=-S,\quad \left(\frac{\partial^2 G}{\partial T^2}\right)_{T_0}=-\left(\frac{\partial S}{\partial T}\right)_{T_0}\equiv G_2,$$

and substituting Eq. (5) into Eq. (8), one obtains

$$G_{\mathrm{eff}}=(H_f^{1v}+H_m^{1v})_{T_0}-\tfrac{1}{2}G_2(T^2-T_0^2). \qquad (9)$$

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This equation may be used to evaluate the temperature dependence of the diffusion activation energy. Since $S=S_f^{1v}+S_m^{1v}$ and S_f^{1v} is nearly temperature-independent as discussed above,

$$G_2=-\left(\frac{\partial S}{\partial T}\right)_{T_0}=-\left(\frac{\partial S_m^{1v}}{\partial T}\right)_{T_0}=-\frac{1}{T_0}\left(\frac{\partial H_m^{1v}}{\partial T}\right)_{T_0}$$

is a measure of the change in motion enthalpy and entropy with temperature.

The values of H_f^{1v} and the H_m^{1v} values determined from the diffusion data may be used to estimate G_2. Since the straight lines drawn previously in Figs. 1 and 2 are only approximations to the curves, the corresponding enthalpies are assigned to temperatures near the extremes. The motion enthalpy of quenched-in defects in Au, measured at room temperature, is 0.71 eV and is interpreted here as H_m^{1v} at that temperature. Since $H_f^{1v}=0.97$ eV and is temperature-independent, an additional point of $Q=1.68$ eV at room temperature in Au can be included. One obtains $G_2\approx-1.6\times10^{-7}$ eV/°K^2 in Au and $G_2\approx-1.2\times10^{-6}$ eV/°K^2 in Al.

There is at present no other information in fcc metals with which these values of G_2 may be compared. The estimated value[38] of G_2 for the diffusion of C in Fe is much less than the current values; however, it is uncertain that this is a good example of a temperature-dependent activation energy, since very reasonable results are obtained using a two-site model for diffusion in the Fe-C system.[39]

Of course, one cannot exclude a divacancy contribution to diffusion at high temperatures in Al and Au. An upper limit for this contribution may be obtained by setting an upper limit for the binding enthalpy at 0.3 eV, the highest commonly quoted value. Using Eq. (3), and the enthalpy and entropy values quoted above, the calculated monovacancy abundances in Al and Au are 86 and 96%, respectively. Using these values and Eq. (2), a ratio of D_1/D_2 may be calculated at the melting point. This gives D_1/D_2 as 24 in Al and 16 in Au. This calculation was made by assuming $(G_m^{1v}-G_m^{2v})$ to be temperature-independent; however, other reasonable values for G_m^{2v} do not change D_1/D_2 appreciably.

This indicates a divacancy contribution to the observed diffusion rate which is about 50 times less than is necessary to explain all of the curvature in Al. In Au, the corresponding factor is five. This verifies that the temperature dependence in the motion enthalpy of single vacancies could be an important factor in causing the observed temperature dependence of the activation for self-diffusion.

TABLE II. Best values for formation and motion enthalpies of single vacancies as a function of temperature.

H_f^{1v}	H_m^{1v}
Aluminum	
0.76 eV; 300–660°C	0.46 eV; 225–325°C
	0.72 eV; 500–650°C
Gold	
0.97 eV; 550–1030°C	0.71 eV; 25°C
	0.75 eV; 600–750°C
	0.83 eV; 875–1025°C

CONCLUSIONS

In summary, it is concluded that:

(1) The experimental diffusion data in Al and Au cannot be represented by a straight line on a $\log D$ versus $1/T$ plot.

(2) The observed increase with temperature in the slope of the diffusivity curve cannot be explained by a divacancy contribution alone with reasonable values of the divacancy binding enthalpy.

(3) A consistent explanation of the increase in slope with temperature is obtained by postulating a temperature-dependent motion enthalpy for single vacancies.

(4) In quenching and annealing studies, one should not compare the enthalpy values obtained with high-temperature diffusion data to identify the species involved.

The best experimental values for the enthalpy of formation and motion are given in Table II where the room-temperature value for the motion energy of a single vacancy in Au is taken from quenching studies.

The possible temperature dependence of H_m^{1v} has not been investigated in theoretical models. Several models could be proposed to explain this effect, including ones related to relaxation around a vacancy and ones related to the temperature dependence of the excitation of phonon modes.[40] The detailed calculation of migration enthalpies of lattice defects involves difficult many-body problems with relatively large uncertainties in the interatomic interactions and their temperature dependences. A complete theoretical investigation of the vacancy-jump process would be necessary to substantiate theoretically the postulated temperature dependence of the migration enthalpy of vacancies.

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