Fast-diffusing substitutionally dissolved impurities in FCC metals: a theoretical approach

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Abstract. For self-diffusion in FCC metals the plot of $\ln D$ against $1/T$ (where D is the diffusion coefficient) is curved. This results from an increasing divacancy contribution to D with rising temperature T. For substitutionally dissolved impurities that diffuse faster than the host atoms, the curvature of $\ln D$ against $1/T$ is drastically reduced, suggesting a small divacancy contribution. In reality, however, the reduced curvature results from the downward curvature of $\ln f_{2.1V}$ against $1/T$ (where $f_{2.1V}$ is the correlation factor).

With the aid of a model calculation it is demonstrated that the divacancy contribution apparently decreases with increasing impurity mass and decreasing migration energy of the impurity.

1. Introduction

The Arrhenius plot of the diffusion coefficient D ($\ln D$ against $1/T$) is more or less curved. For FCC metals this curvature is caused by an increasing contribution of divacancies to the entire diffusion flux (Seeger and Mehrer 1970, Peterson 1978a,b, Mehrer 1978, Neumann 1989). This is valid not only for self-diffusion but also for impurity diffusion. For substitutionally dissolved impurities that diffuse faster than the host atoms, however, the curvature of $\ln D$ against $1/T$ is drastically reduced. This results from the fact that the Arrhenius plot of the correlation factor f_2 of the impurity diffusion reveals a downward curvature in $\ln f_2$ against $1/T$ (Neumann 1987).

In the present paper, we report on model calculations, which demonstrate the influence of the mass m_2 of the impurity and the vacancy migration energy $H_{2.1V}^M$ of the impurity on the curvature of $\ln D$ against $1/T$, the effective diffusion energy Q_2 and the temperature dependence of ΔQ, the difference between the activation energies of impurity diffusion and self-diffusion.

2. The five-frequency model

Impurity diffusion and self-diffusion occur via monovacancies and divacancies, the diffusion coefficient D is given by

$$D_j = D_{j.1V} + D_{j.2V} = D_{j.1V}^0 \exp(-Q_{j.1V}/kT) + D_{j.2V}^0 \exp(-Q_{j.2V}/kT) \qquad (1)$$

where $j = 0, 2$ refer to self-diffusion and impurity diffusion and 1V and 2V to mono-

vacancy and divacancy contributions, respectively. D^0 and Q are the respective pre-exponential factors and diffusion energies. The deviation of the impurity diffusion coefficient D_2 from that of self-diffusion D_0 can be expressed in terms of the five-frequency model (see, e.g., LeClaire 1962)

$$D_{2.iV}/D_{0.iV} = w_{2.iV} w_{4.iV} f_{2.iV}/w_{0.iV} w_{3.iV} f_{0.iV} \tag{2}$$

where $i = 1, 2$ refers to monovacancy and divacancy diffusion, respectively. w_2 and w_0 are the jump frequencies of the impurities and host atoms in the pure lattice, and w_4 and w_3 are the frequencies of host atom jumps that are associative and dissociative with respect to the impurity–vacancy pair, respectively. w_4/w_3 represents the deviation of the vacancy concentration close to the impurity from that in the pure lattice. f_2 and f_0 are the correlation factors of the impurity diffusion and self-diffusion, respectively ($f_{0.1V} = 0.781$; $f_{0.2V} = 0.458$). f_2 is a function of temperature, which can be approximated by

$$f_{2.1V} = (2w_{1.1V} + 7F_{1V}w_{3.1V})/(2w_{1.1V} + 2w_{2.1V} + 7F_{1V}w_{3.1V}) \tag{3}$$

for monovacancy diffusion (Manning 1962) and by

$$f_{2.2V} = F_{2V}w_{3.2V}/(2w_{2.2V} + F_{2V}w_{3.2V}) \tag{4}$$

for diffusion of non-dissociating divacancies (Mehrer 1972). $w_{1.1V}$ is the jump frequency of a host atom that is the nearest neighbour of the impurity before and after the jump. F_{1V} and F_{2V} are partial correlation factors ($7F_{1V} \simeq 5.15$; $F_{2V} \simeq 0.85$).

For slow-diffusion impurities, f_2 tends towards unity and is almost temperature independent. For fast-diffusing impurities, however, f_2 strongly increases with rising temperature (see § 3). In a forced Arrhenius plot the temperature function of f_2 can be approximated by

$$f_2(T) = f_2^0(\bar{T}) \exp[C(\bar{T})/kT] \tag{5}$$

where the pre-exponential factor f^0 and the 'activation energy' C are averages for the temperature range under consideration.

The temperature function of w obeys an Arrhenius-type equation

$$w = \nu \exp(S^M/k) \exp(-H^M/kT) \tag{6}$$

where H^M and S^M are the migration energy and entropy, respectively. ν is a lattice frequency. Thus the temperature increment in equation (2) is given by

$$\Delta Q_{iV} = \Delta H_{iV}^M + \Delta H_{iV}^F - C_{iV}(\bar{T}) \tag{7}$$

where $\Delta H_{iV}^F = \Delta H_{4.iV}^M - \Delta H_{3.iV}^M$ is the negative value of the binding energy between the impurity and vacancy or the vacancy pair, respectively, and $\Delta H_{iV}^M = H_{2.iV}^M - H_{0.iV}^M$.

3. The calculation of the impurity diffusion coefficient

The impurity diffusion coefficient can be calculated, if all ΔH, ΔS and $\nu_{k.iV}/\nu_{0.iV}$ can be determined. Starting with the approximation of ΔH_{1V}^M (Neumann and Hirschwald 1973) or ΔH_{1V}^F (LeClaire 1962), respectively, a suitable potential function is needed to calculate the other $\Delta H_{k.iV}^M$ values ($k = 1, 3, 4$). In the T_m model (Neumann and Hirschwald

1973, 1974) a Morse potential (Neumann *et al* 1972) is used to estimate the values of $\Delta H^M_{k.iV} = H^M_{k.iV} - H^M_{0.iV}$ in the form

$$\Delta H^M_{k.iV} = K_{k.iV} \, \Delta H^M_{1V}. \tag{8}$$

This results in $K_{1.1V} = 0.19$, $K_{3.1V} = -0.16$ and $K_{4.1V} = 0.01$ for monovacancy diffusion (Neumann and Hirschwald 1973). For divacancy diffusion it was assumed that $\Delta H^M_{2V} \simeq 0.7 \, \Delta H^M_{1V}$, $\Delta H^F_{2V} \simeq 2 \, \Delta H^F_{1V}$ and $\Delta H^M_{3.2V} \simeq \Delta H^M_{3.1V}$ (Neumann 1987).

The entropy differences are estimated on the basis of an approach by Wert and Zener (1949), resulting in (Neumann and Hirschwald 1974)

$$\Delta S^M_{1V} = \beta \, \Delta H^M_{1V}/T_{m0} \tag{9}$$

where β is the temperature dependence of the shear modulus and T_{m0} is the melting temperature of the host. The other entropy differences are approximated according to

$$\Delta S^M_{k.iV} = K_{k.iV} \, \Delta S^M_{1V}. \tag{10}$$

The lattice frequences $\nu_{k.iV}$ associated with the $w_{k.iV}$ jumps are assumed to be equal for all host atom jumps, i.e. $\nu_{k.iV} = \nu_{0.iV}$ ($k = 1, 3, 4$). The lattice frequency associated with the impurity jump is assumed to differ from that of the host atom jump by (Neumann and Hirschwald 1974)

$$\nu_{2.iV}/\nu_{0.iV} = [(m_0/m_2)q]^{1/2}. \tag{11}$$

m_0 and m_2 are the masses of host atoms and impurities, respectively. In the T_m model, q is approximated by $q = T_{m2}/T_{m0}$, where T_{m2} is the melting temperature of the solute.

The application of these approximations permits the calculation of $D_{2.1V}(T)$ and $D_{2.2V}(T)$ and thus of $D_2(T)$. Comparison of theoretical and experimental data reveals good agreement for a number of impurity diffusion systems (Neumann 1987). In particular, for fast-diffusing elements of the IVa, Va and VIa group, however, the T_m model underestimates the diffusivities.

In order to characterise the peculiarities of the fast diffusivity, model calculations are performed. The inserted data are chosen so that the results are typical for diffusion in noble metals. The following parameter values are assumed: $\Delta H^M_{1V} = -0.2, -0.3$ and -0.4 eV and $m_2/m_0 = 3, 1$ and $\frac{1}{3}$. Furthermore $\beta = 0.4$ is used for the calculation of ΔS and $H^M_{0.1V} = 1$ eV for the determination of q from $\Delta H^M_{1V} = (H^M_{0.1V}/2)(q - 1)$, which is needed to approximate $\nu_{2.iV}/\nu_{0.iV}$.

With the aid of equations (2)–(4), (6) and (8)–(11), $D_{2.iV}/D_{0.iV}$ can be calculated. These values are recalculated to $D_{2.1V}$ and $D_{2.2V}$ by use of the self-diffusion parameters for Ag (table 1). The least-squares fit of $D_{2.1V}(T)$ and $D_{2.2V}(T)$ according to $D = D^0 \exp(-Q/kT)$ leads to the respective pre-exponential factors and activation energies. Furthermore, the double-exponential fit of $D_2(T)$ according to equation (1) (by applying the routine of Morrison (1975)) leads to the monovacancy and apparent divacancy parameters. This can be expressed by

$$D_2 = D^{extr}_{2.1V} + D^{app}_{2.2V}. \tag{12}$$

$D^{extr}_{2.1V}$ is the monovacancy diffusion coefficient extrapolated to higher temperatures. $D^{extr}_{2.1V}$ is overestimated, as the downward curvature of $\ln f_{2.1V}$ against $1/T$ is not taken into consideration in the two-exponential fit. As a consequence, the divacancy contribution and thus the apparent divacancy diffusion coefficient $D^{app}_{2.2V}$ is underestimated. This means that the true divacancy contribution is partly compensated by the downward curvature of $\ln f_{2.1V}$ against $1/T$.

Table 1. Calculated monovacancy and divacancy diffusion energies Q and pre-exponential factors D^0 compared with the parameters obtained from the double-exponential fit of the calculated $D_2(T)$. The column labelled $D_{2,2V}/D_2$ is for $T = T_{m0}$. The self-diffusion parameters, i.e. $\Delta H^M_{1V} = 0$, are taken from Neumann and Tölle (1986).

ΔH^M_{1V} (eV)	m_2/m_0	Calculated quantities for $\bar{T} = 0.85\,T_{m0}$						Double-exponential fit of $D_2(T)$				$D_{2,2V}/D_2$	
		$D^0_{2,1V}$ (cm²s⁻¹)	$Q_{2,1V}$ (eV)	$D^0_{2,2V}$ (cm²s⁻¹)	$Q_{2,2V}$ (eV)	D^0_2 (cm²s⁻¹)	Q_2 (eV)	$D^0_{2,1V}$ (cm²s⁻¹)	$Q_{2,1V}$ (eV)	$D^{0,\mathrm{app}}_{2,2V}$ (cm²s⁻¹)	$Q^{\mathrm{app}}_{2,2V}$ (eV)	Calculated	Apparent
−0.4	3	0.016	1.540	7.3	2.21	0.11	1.687	0.068	1.649	31000	3.22	0.47	0.14
−0.4	1	0.032	1.586	10.9	2.24	0.19	1.717	0.086	1.660	45	2.46	0.43	0.22
−0.4	$\frac{1}{3}$	0.057	1.625	14.4	2.25	0.28	1.742	0.094	1.664	8.2	2.23	0.40	0.30
−0.3	3	0.018	1.577	8.0	2.23	0.14	1.729	0.064	1.670	3300	2.96	0.48	0.21
−0.3	1	0.035	1.616	11.7	2.26	0.22	1.751	0.093	1.686	268	2.66	0.45	0.23
−0.3	$\frac{1}{3}$	0.061	1.649	15.2	2.27	0.32	1.770	0.115	1.695	40	2.42	0.41	0.27
−0.2	3	0.019	1.621	8.2	2.26	0.18	1.782	0.046	1.681	148	2.61	0.51	0.33
−0.2	1	0.035	1.647	12.1	2.28	0.26	1.794	0.076	1.700	148	2.59	0.47	0.31
−0.2	$\frac{1}{3}$	0.060	1.673	15.7	2.29	0.33	1.803	0.109	1.714	91	2.52	0.43	0.30
0	1					0.61	1.954	0.055	1.773	15.1	2.35	0.54	0.54

Table 2. Comparison of the calculated monovacancy diffusion energy differences ΔQ_{1V} for $\bar{T} = 0.55 \, T_{m0}$ and $\bar{T} = 0.85 \, T_{m0}$ with the effective ΔQ for $\bar{T} = 0.85 \, T_{m0}$.

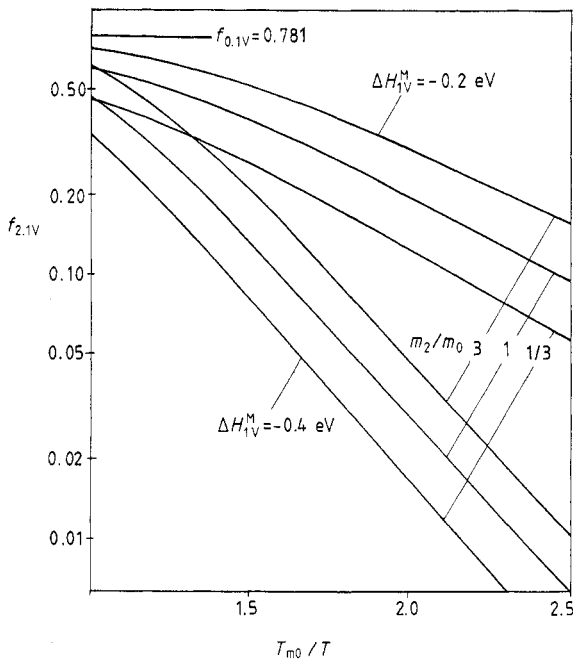| ΔH_{1V}^M (meV)	ΔH_{1V}^F (meV)	m_2/m_0	ΔQ_{1V} (0.55 T_{m0}) (meV)	ΔQ_{1V} (0.85 T_{m0}) (meV)	ΔQ (0.85 T_{m0}) (meV)
-400	-68	3	-124	-233	-267
-400	-68	1	-113	-187	-237
-400	-68	$\frac{1}{3}$	-110	-148	-212
-300	-51	3	-103	-196	-225
-300	-51	1	-87	-158	-203
-300	-51	$\frac{1}{3}$	-78	-124	-184
-200	-34	3	-92	-153	-172
-200	-34	1	-73	-127	-160
-200	-34	$\frac{1}{3}$	-59	-101	-151

Figure 1. Calculated temperature functions of the correlation factor $f_{2.1V}$.

The results of the model calculations are listed in tables 1 and 2 and are shown in figures 1 and 2. The columns labelled $D_{2.1V}^0$ and $Q_{2.1V}$ and labelled $D_{2.2V}^0$ and $Q_{2.2V}$ in table 1 are the calculated monovacancy and divacancy parameters for the temperature range from $0.7 \, T_m$ to T_m. The columns labelled D_2^0 and Q_2 give the effective diffusion parameters for this temperature range, where the effective diffusion energy corresponds to

$$Q_2(T) = (D_{2.1V}/D_2)Q_{2.1V} + (D_{2.2V}/D_2)Q_{2.2V}. \tag{13}$$

Because of the non-linearity of $\ln f_{2.1V}$ against $1/T$ (see figure 1), $Q_{2.1V}$ and $D_{2.1V}^0$ depend on T. The parameters calculated for the temperature range from $0.4 \, T_m$ to $0.7 \, T_m$
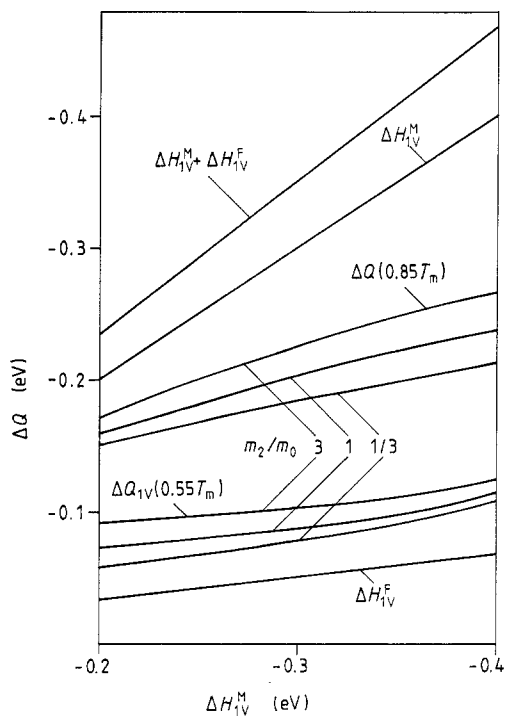
Figure 2. Comparison of ΔQ-values calculated for different temperature ranges with ΔH_{1V}^{M} and ΔH_{1V}^{F}.

are almost identical with those obtained from the two-exponential fit (see columns labelled $D_{2.1V}^{0}$ and $Q_{2.1V}$). The columns labelled $D_{2.2V}^{0,\text{app}}$ and $Q_{2.2V}^{\text{app}}$ contain the apparent divacancy parameters and in the columns labelled $D_{2.2V}/D_2$ the calculated divacancy contributions at the melting temperature are compared with the apparent contributions deduced from the two-exponential fit.

For the double-exponential fit, 13 calculated D_2 values between $0.4\,T_{\mathrm{m}}$ and T_{m} are used. Owing to the non-linearity of $\ln f_2$ against $1/T$ the standard deviation σ is larger than zero. σ ranges from 0.008 to 0.02. σ increases with decreasing apparent divacancy contribution from $\Delta H_{1V}^{M} = -0.2\,\mathrm{eV}$, $m_2/m_0 = \frac{1}{3}$, to $\Delta H_{1V}^{M} = -0.4\,\mathrm{eV}$, $m_2/m_0 = 3$. While the monovacancy parameters reveal minimal uncertainties, the error limits of the apparent divacancy parameters increase with decreasing apparent divacancy contribution. The results are $Q_{2.2V} = 2.52 \pm 0.06\,\mathrm{eV}$ for $\Delta H_{1V}^{M} = -0.2\,\mathrm{eV}, m_2/m_0 = \frac{1}{3}$, and $Q_{2.2V} = 3.22 \pm 0.40\,\mathrm{eV}$ for $\Delta H_{1V}^{M} = -0.4\,\mathrm{eV}, m_2/m_0 = 3$, respectively.

In table 2 and figure 2 the calculated ΔQ_{1V}-values for the temperature ranges from $0.4\,T_{\mathrm{m}}$ to $0.7\,T_{\mathrm{m}}$ and from $0.7\,T_{\mathrm{m}}$ to T_{m} are compared with the effective ΔQ for the upper temperature range. The self-diffusion energies Q_0 and $Q_{0.1V}$ needed to calculate $\Delta Q = Q_2 - Q_0$ and $\Delta Q_{1V} = Q_{2.1V} - Q_{0.1V}$ are given in the last row of table 1.

The calculated values for Q and ΔQ are valid for impurity diffusion in Ag. For diffusion in Cu and Au the absolute values are about 10% larger and smaller, respectively. Moreover, the principal trends should be of general validity for substitutional impurities in all FCC metals.

4. Conclusions

For the diffusion behaviour of fast-diffusing substitutionally dissolved impurities in FCC metals a number of trends can be deduced from the present model calculations.

(i) The calculated divacancy contribution at the melting temperature is much larger than that estimated from the two-exponential fit of $D_2(T)$ (see table 1). This results from the fact that the downward curvature of $\ln f_{2.1V}$ against $1/T$ partly compensates the upward curvature of $\ln D_2$ against $1/T$, which is caused by the divacancy contribution.

(ii) The effect of the apparently reduced divacancy contribution increases with increasing amount of ΔH_{1V}^{M} and increasing m_2/m_0 (see table 1). As a consequence, nearly linear Arrhenius plots over several orders of magnitude can result. Experimentally this was observed for In in Ag (Tomizuka and Slifkin 1954, Mehrer and Weiler 1984), Te in Ag (Geise *et al* 1987) and Ge in Ni (Mantl *et al* 1983).

(iii) The consequence of the drastic reduction in the curvature of $\ln D_2$ against $1/T$ is an increase in the apparent divacancy parameters $D_{2.2V}^{0,\text{app}}$ and $Q_{2.2V}^{\text{app}}$ (see table 1). Thus, comparison of theoretical and experimental $Q_{2.2V}$ becomes meaningless.

(iv) In the lower-temperature range ($\bar{T} = 0.55\ T_{m0}$), ΔQ_{1V} is nearly independent of ΔH_{1V}^{M} (see table 2). Although ΔH_{1V}^{M} differs by 200 meV, the differences in ΔQ_{1V} are not larger than 30–50 meV depending on m_2/m_0. This results from the fact that for large $w_{2.1V}/w_{0.1V}$ (i.e. large ΔH_{1V}^{M}) the denominator of $f_{2.1V}$ is close to $w_{2.1V}$ and thus $D_{2.1V}/D_{0.1V}$ becomes almost independent of ΔH_{1V}^{M}.

(v) A further consequence is that $D_{2.1V}$ becomes nearly mass independent in the lower-temperature range, at least for large ΔH_{1V}^{M} (see table 1). Experimentally this was observed for Se and Te diffusion in Cu (Rummel and Mehrer 1989). While Q_2 is 1.7 eV in both cases, D_2^0 merely differs by a few per cent ($D_2^0(\text{Se}) = 1.0\ \text{cm}^2\ \text{s}^{-1}$; $D_2^0(\text{Te}) = 0.97\ \text{cm}^2\ \text{s}^{-1}$).

(vi) In the high-temperature range ($\bar{T} = 0.85\ T_{m0}$) as well, ΔQ_{1V} differs by not more than 50–80 meV (depending on m_2/m_0), although the ΔH_{1V}^{M}-values are -200 meV and -400 meV, respectively (see table 2). Obviously, ΔQ_{1V} (0.85 T_{m0}) is larger than ΔQ_{1V} (0.55 T_{m0}); this is a consequence of the downward curvature of $\ln f_{2.1V}$ against $1/T$ so that $C(\bar{T})$ also decreases with rising temperature.

(vii) Table 2 reveals that ΔQ_{1V} (0.85 T_{m0}) and the effective ΔQ (0.85 T_{m0}) (including the divacancy contributions) differ by not more than 20–65 meV. This justifies comparison of the calculated ΔQ_{1V} (0.85 T_{m0}) and experimental ΔQ (0.85 T_{m0}) as an acceptable first approximation (LeClaire 1962, Neumann and Hirschwald 1973, 1974). On the contrary, the fact that $C(\bar{T})$ compensates a large part of ΔH_{1V}^{M} (see equation (7)) can simulate good agreement between theory and experiment, although the calculated ΔH_{1V}^{M} is erroneous.

(viii) The compensation effect ($\Delta H_{1V}^{M} - C$) leads to the result that, in the lower temperature range, ΔQ_{1V} is not much larger than the binding energy between impurity and vacancy, i.e. $\Delta H_{1V}^{B} = -\Delta H_{1V}^{F}$ (see table 2 and figure 2). Thus ΔQ_{1V} (0.55 T_{m0}) is an acceptable upper limit for ΔH_{1V}^{B}. In general, ΔH_{1V}^{B} is determined with the aid of resistivity measurements or PAS investigations on dilute alloys. In the case of a pronounced attraction between vacancy and impurity this leads to a cluster formation in that more than one impurity is in the nearest-neighbour shell of the vacancy (Dorn and Mitchell 1966). As a consequence, the measured $\Delta H_{1V}^{B}(\text{eff})$ represents the binding energy of the cluster. Thus, $-\Delta Q_{1V}$ (0.55 T_{m0}) is a more realistic upper limit for ΔH_{1V}^{B} than the values deduced from investigations on dilute alloys (Neumann 1987).

In summarising the present results, it can be stated that for fast-diffusing substitutional impurities the upward curvature of $\ln D_2$ against $1/T$ caused by the divacancy contribution can almost vanish as the result of the downward curvature of $\ln f_{2.1V}$ against

$1/T$. Hence the linearity of ln D_2 against $1/T$ cannot be considered as proof of the non-existence of a divacancy contribution. This should be valid for all FCC metals and thus for diffusion in Al as well (see, however, the work by Peterson and Rothman (1970) and Mundy (1987)). In particular, as, in Al, m_2/m_0 ranges from 2 to 6, a small apparent divacancy contribution has to be expected (see table 1).

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