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COMMENT

Remarks on the comments on the diffusion of Ni and Ge in Ni made by Hadjicontis and co-workers

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Abstract. $g = cB\Omega$ is a good approximation for the temperature function of the diffusion coefficient D . $B(T)\Omega(T)$, however, does not explain the entire curvature of $\ln D$ against $1/T$ and thus is no proof for the contribution of only one defect to D . The application of this relation to the impurity diffusion leads to an additional error due to an incorrect assumption with respect to the impurity diffusion entropy.

1. Introduction

Varotsos *et al* (1978) have proposed an empirical correlation

$$D(T) = a^2 \nu f \exp[-cB(T)\Omega(T)/k_B T] \quad (1)$$

which describes the temperature function of the diffusion coefficient D with those of the bulk modulus B and the atomic volume Ω . c is assumed to be an empirical temperature-independent constant. a is the lattice constant, ν is a lattice frequency associated with the diffusion jump and f is the correlation factor. The application to self-diffusion (Varotsos and Alexopoulos 1980) and impurity diffusion in metals (Alexopoulos and Varotsos 1981) reveals that equation (1) is a good first approximation.

In general the Arrhenius plot of D ($\ln D$ against $1/T$) is more or less curved. This curvature can be explained by the competition of at least two diffusion mechanisms (two-defect model) (see, e.g., Mehrer 1978, Neumann 1989) or by a pronounced temperature dependence of the diffusion energies and entropies (one-defect model) (Gilder and Lazarus 1975).

If the temperature function of $B\Omega$ is non-linear, this leads to a temperature dependence of the diffusion enthalpy h :

$$h = cB\Omega - cT \partial(B\Omega)/\partial T. \quad (2)$$

According to equation (2) in most cases h increases with rising temperature. This was considered as a proof for the existence of only one defect contributing to D . It can be demonstrated, however, that at least for FCC metals the temperature dependence of h according to equation (2) underestimates the curvature of $\ln D$ against $1/T$.

In the simplest manner a temperature dependence of enthalpy h and entropy s can be expressed by (see, e.g., Seeger and Mehrer 1970)

$$h(T) = h(T_0) + 2\alpha k_B(T - T_0) \quad (3a)$$

$$s(T) = s(T_0) + 2\alpha k_B \ln(T/T_0) \quad (3b)$$

where T_0 is a reference temperature. If two defects are contributing to the diffusivity, D is given by

$$D = D_1 + D_2 = D_1^0 \exp(-h_1/k_B T) + D_2^0 \exp(-h_2/k_B T). \quad (4)$$

From the measured temperature function of D a distinction between the one-defect and the two-defect model is not possible, as the resulting standard deviation is nearly equal for the fitting procedures according to equation (4) and $D = a^2 \nu f \exp[-g(T)/k_B T]$ with $h(T)$ and $s(T)$ according to equation (3), respectively.

2. The application of the $B\Omega$ model to self-diffusion and impurity diffusion in metals

Recently, Hadjicontis *et al* (1988) have applied equation (1) to describe the diffusivity of Ni and Ge in Ni. For the calculation of $D(T)$ the bulk moduli measured by Alers *et al* (1960) were used. The calculated $D(T)$ are compared with self-diffusion coefficients measured by Bakker (1968) and Maier *et al* (1976) and for Ge diffusion in Ni with those measured by Mantl *et al* (1983). Hadjicontis *et al* (1988) assumed a temperature-independent value of $\partial(B\Omega)/\partial T$ equal to $-3.6 \times 10^{-22} \text{ J K}^{-1}$. The resulting temperature-independent diffusion energies are 3.00 eV and 2.77 eV for Ni and Ge diffusion in Ni, respectively. As the measured diffusion energies are 2.74 eV for Ge in Ni and range from 2.91 to 3.04 eV according to the estimation of Maier *et al* (1976), Hadjicontis *et al* (1988) conclude favourable agreement between theory and experiment.

The analysis of the self-diffusion coefficients of Ni according to equation (4) (Neumann and Tölle 1986), however, leads to an increase in the effective diffusion enthalpy h_{eff} from 2.87 eV at 900 K to 3.13 eV at 1700 K (table 1). According to equation (3) this corresponds to $\alpha = 1.9$, which is much larger than the expected upper limit of about 0.2 (see, e.g., Peterson 1978). In reality, the temperature function of $B\Omega$ corresponds to a temperature gradient $\partial(B\Omega)/\partial T$ ranging from about $-3.4 \times 10^{-22} \text{ J K}^{-1}$ at 900 K to about $-3.8 \times 10^{-22} \text{ J K}^{-1}$ at 1700 K. This leads to a temperature dependence of h , which, however, is too small to explain the entire curvature of $\ln D$ against $1/T$ for the Ni self-diffusion (see table 1).

The situation is similar for self-diffusion in copper, where the temperature dependence of h calculated from $B\Omega$ (Varotsos and Alexopoulos 1980) is distinctly smaller than that of h_{eff} obtained from the two-exponential fit according to equation (4) (Neumann and Tölle 1986) (see table 1).

For Ge diffusion in Ni the Arrhenius plot is linear over more than six orders of magnitude in D . This corresponds to a temperature-independent diffusion energy in agreement with the result obtained by Hadjicontis *et al* (1988). The more realistic T -function of $\partial(B\Omega)/\partial T$, however, suggests an increase in h with increasing T (see table 1), which is in contrast with the experimental result. The observed linearity of $\ln D$ against $1/T$, on the contrary, is in agreement with the fact that for rapidly diffusing impurities the upward curvature of $\ln D$ against $1/T$ (resulting from $D_2/D > 0$ or $\alpha > 0$) is nearly cancelled by the downward curvature of $\ln f$ against $1/T$ (Neumann 1987).

Table 1. Comparison of the diffusion energies calculated from $g = cB\Omega$ and from the two-exponential fit.

System	T (K)	$h_{B\Omega}$ (eV)	h_{eff} (eV)
Ni in Ni	900	2.965 ^a	2.87 ^b
Ni in Ni	1300	3.00	2.89
Ni in Ni	1700	3.045	3.13
α		0.6	1.9
Ge in Ni	900	2.73 ^a	2.74 ^c
Ge in Ni	1300	2.77	2.74
Ge in Ni	1700	2.81	2.74
α		0.54	0
Cu in Cu	700	2.134 ^d	2.065 ^b
Cu in Cu	1000	2.135	2.14
Cu in Cu	1300	2.155	2.24
α		0.2	1.7

^a $h_{B\Omega}$ for Ni and Ge in Ni calculated assuming an increase in $\partial(B\Omega)/\partial T$ from -3.4×10^{-22} to $-3.8 \times 10^{-22} \text{ J K}^{-1}$.

^b According to Neumann and Tölle (1986).

^c According to Mantl *et al* (1983).

^d According to Varotsos and Alexopoulos (1980).

In addition to the objections against the connection between the curvature of $\ln D$ against $1/T$ and the T -function of $B\Omega$ and the disregard of the T -dependence of f , there are further important objections against the applicability of

$$g = cB\Omega \tag{5}$$

to the impurity diffusion in metals (Neumann 1986, Neumann and Beke 1989). Alexopoulos and Varotsos (1981) have assumed that equation (5) is valid for self-diffusion as well as for impurity diffusion in that merely different values of c describe the respective $g(T)$. This assumption suggests that s/h is a constant:

$$s/h = [\partial(B\Omega)/\partial T]/[B\Omega - T\partial(B\Omega)/\partial T] = K \tag{6}$$

which is independent of whether vacancy formation or migration, self-diffusion or impurity diffusion is considered. In particular, this means that

$$\Delta s = K \Delta h \tag{7}$$

with $h = h_i - h_s$ and $s = s_i - s_s$ (the subscripts i and s refer to impurity diffusion and self-diffusion, respectively). As the frequency factor is given by $D^0 = a^2\nu f \exp(s/k_B)$, this means that

$$\ln[(D_i^0/D_s^0)(m_i/m_s)^{1/2}] = \Delta s/k_B = K \Delta h/k_B \tag{8}$$

on the assumptions that $f_i = f_s$ and $\nu_i/\nu_s = (m_s/m_i)^{1/2}$ (m_s and m_i are the matrix atom mass and the impurity mass, respectively) and that Δs can be expressed by equation (7).

The proportionality between $\ln(D_i^0 m_i^{1/2})$ and h_i is well known. The gradient, however, is larger than K/k_B , namely about $2K/k_B$ (Pelleg 1966). This discrepancy was explained in detail by Neumann and Hirschwald (1974) and Neumann (1986).

Recently, Grammatikakis *et al* (1988) have applied equation (8) to impurity diffusion in aluminium. They fitted $\ln[(D_i^0/D_s^0)(m_i/m_s)^{1/2}] = A_i$ against h_i with the slope K/k_B obtained from equation (6). The fact that this slope is wrong can be easily demonstrated. $A = 0$ corresponds to $h_i = h_s$. According to their figure 1, $A = 0$ leads to $h_s = 0.5$ eV instead of the inserted experimental value of $h_s = 1.47$ eV (and $D_s^0 = 1.71$ cm² s⁻¹) (Lundy and Murdock 1962). The line with the slope K/k_B passing through $h = 1.47$ eV at $A = 0$ does not fit any of the experimental data points A_i, h_i .

3. Conclusions

The present considerations lead to the following conclusions: $g = cB\Omega$ is an acceptable approximation for the description of the temperature function of D for self-diffusion in metals. This also holds for impurity diffusion, although the temperature dependence of the correlation factor is disregarded and although the assumption that $s/h = K$ is valid for self-diffusion as well as for impurity diffusion is wrong. The main consequence suggested by this model, namely that the good approximation of $D(T)$ is a proof of the one-defect model, however, must be rejected.

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