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The correlation factor of impurity diffusion in body-centred cubic metals for mixed nearest- and next-nearest-neighbour monovacancy jumps

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Abstract. The correlation factor f_2 of impurity diffusion in body-centred cubic metals is calculated assuming the competition of nearest- and next-nearest-neighbour monovacancy jumps. A four-frequency model in which only the impurity jump frequencies differ from those of the host atoms is considered. f_2 is calculated as a function of temperature for different impurity migration energies and impurity masses.

A comparison of f_2 with experimental data shows qualitative agreement with the temperature function of the isotope effect for chromium diffusion in tungsten, thus supporting the hypothesis of high-temperature contributions of next-nearest-neighbour vacancy jumps in group V and VI metals.

1. Introduction

The diffusion mechanism in the body-centred cubic (BCC) metals of the groups V and VI has to be considered as an open question [1]. The strong curvature of the Arrhenius plot ($\ln D$ against $1/T$) of the diffusion coefficient D was explained by the competition of two diffusion mechanisms with different activation energies or by the temperature dependence of diffusion energies and entropies, respectively. It is well known that, in the lower-temperature range, material transport occurs via monovacancy jumps. In the temperature range close to the melting point, contributions of divacancies [2], self-interstitials [3], or next-nearest-neighbour (NNN) monovacancy jumps [4] are assumed to dominate the diffusivity in group V and VI metals. On the contrary, it was proposed that the phonon mode softening, which is responsible for the distinct enhancement of the diffusivity in the lower-temperature range of the BCC phase of group IV metals, explains the curvature of $\ln D$ versus $1/T$ in group V and VI metals as well [5].

It could be demonstrated that the calculated diffusion energies for V, Cr and W, the heat of thermotransport in V, and the measured temperature function of the isotope effect in Nb are compatible with the concept of nearest-neighbour (NN) and NNN monovacancy jumps [1, 4].

For that purpose the temperature function of the correlation factor $f_0(T)$ was calculated for the self-diffusion in BCC metals taking into account the competition of

monovacancy jumps via NN and NNN sites [6]. $f_0(T)$ was calculated applying a Monte Carlo simulation as well as the method of Compaan and Haven [7].

In the present paper the correlation factor $f_2(T)$ of impurity diffusion is calculated for substitutionally dissolved impurities in BCC metals using a Monte Carlo simulation. $f_2(T)$ depends on the jump frequency ratio $w_2^{\text{NNN}}/w_2^{\text{NN}}$ of NNN to NN neighbour jumps. $f_2(T)$ is determined for different migration energies and different impurity masses.

Some simplifying assumptions are made for the vacancy jump frequencies, which are deduced from experimental results of self-diffusion. Assumptions of a special impurity diffusion model are avoided in this first approximation.

2. The four-frequency model of the impurity diffusion in body-centred cubic metals

In the present approximation it is assumed that only the jump frequencies w_2^{NNN} and w_2^{NN} of the impurities differ from the jump frequencies w_0^{NNN} and w_0^{NN} of the host atoms. In this simple four-frequency model it is assumed that none of the host atom jumps is influenced by the presence of the impurities.

The experimental self-diffusion data can be analysed according to

$$D_0(T) = D_{01} + D_{02} = D_{01}^0 \exp(-Q_{01}/kT) + D_{02}^0 \exp(-Q_{02}/kT). \quad (1)$$

For group V and VI metals (except Ta) these analyses lead to the following approximations for the diffusion energies Q and pre-exponential factors D^0 [8]:

$$Q_{01}/T_m \simeq 1.5 \text{ meV K}^{-1} \quad (2a)$$

$$Q_{02}/T_m \simeq 2.0 \text{ meV K}^{-1} \quad (2b)$$

$$D_{02}^0/D_{01}^0 \simeq 1000. \quad (2c)$$

When additionally taking into account the results of quenching investigations as well as positron annihilation studies, this leads to the following approximation for the vacancy formation energy H_{1V}^F [9]:

$$H_{1V}^F/T_m \simeq 1.0 \text{ meV K}^{-1}. \quad (3)$$

Since $Q = H^F + H^M$, this means that for NN and NNN jumps the vacancy migration energies are

$$H_{0NN}^M/T_m \simeq 0.5 \text{ meV K}^{-1} \quad (4a)$$

$$H_{0NNN}^M/T_m \simeq 1.0 \text{ meV K}^{-1}. \quad (4b)$$

The self-diffusion coefficient for mixed NN and NNN monovacancy jumps is given by [4]

$$D_0(T) = a^2 c_{1V} f_0(T) (w_0^{\text{NN}} + w_0^{\text{NNN}}) \quad (5)$$

where a is the lattice constant and c_{1V} is the vacancy concentration. From equations (1) and (5) it follows that

$$w_0^{\text{NNN}}/w_0^{\text{NN}} = D_{02}/D_{01} = (D_{02}^0/D_{01}^0) \exp[-(Q_{02} - Q_{01}/kT)] \quad (6)$$

with

$$Q_{02} - Q_{01} \approx H_{0NN}^M \quad (7)$$

deduced from equation (4).

The vacancy jump frequency w is given by

$$w = \nu \exp(S^M/k) \exp(-H^M/kT). \quad (8)$$

In the present calculations it is simply assumed that the vacancy migration entropies S^M are equal for impurity diffusion and self-diffusion ($\Delta S_{NN}^M = \Delta S_{NNN}^M = 0$). Furthermore the lattice frequency ratio ν_2/ν_0 is expressed by $(m_0/m_2)^{1/2}$. This leads to the equations

$$w_2^{NN}/w_0^{NN} = (m_0/m_2)^{1/2} \exp(-\Delta H_{NN}^M/kT) \quad (9)$$

$$w_2^{NNN}/w_0^{NNN} = (m_0/m_2)^{1/2} \exp(-2 \Delta H_{NN}^M/kT). \quad (10)$$

3. The method of calculation

The method is based on the ideas developed by Bakker [10] and de Bruin *et al* [11], to determine, for the case of a single atomic jump mechanism by monovacancies, the net probability of an atomic jump in the opposite direction relative to its preceding jump. Their starting point was an equation derived by Mullen [12]. When more than one diffusion mechanism is operative, a similar method can be used. However, in that case the starting point can no longer be the equation that Mullen derived. Then we have to use a more general equation derived by Howard [13]. Applying this equation to the case of two jump mechanisms with jump lengths into the x -direction l_1 and l_2 , occurring in fractions c_1 and c_2 of the total number of jumps, the correlation factor for displacements into the x direction is

$$f_x = 1 + 2b \cdot \mathbf{T}_1(1 - \mathbf{T}_1)^{-1} \mathbf{d} \quad (11)$$

with $b = (c_1 l_1^2 + c_2 l_2^2)^{-1}(c_1 l_1, c_2 l_2)$ and

$$\mathbf{d} = \begin{pmatrix} l_1 \\ l_2 \end{pmatrix}.$$

\mathbf{I} is the 2×2 unit matrix and \mathbf{T}_1 is a 2×2 matrix containing the elements t_{ij} , defined by

$$t_{ij} = p_+^{ij} - p_-^{ij} \quad (12)$$

where p_{\pm}^{ij} is the probability that, after the atom has made a jump of type i , its next jump will be of type j with its projection on the x axis into the same or into the opposite direction. Jumps with zero displacements into the x direction are not considered. Substituting

$$\mathbf{S} = \mathbf{T}_1(1 - \mathbf{T}_1)^{-1} \quad (13)$$

and

$$l_1 = 1 \quad l_2 = 2 \quad (14)$$

the lattice parameter being set on 2, for ease of calculation, the equation reduces to

$$f_x = 1 + [2/(c_1 + 4c_2)][c_1(s_{11} + 2s_{12}) + 2c_2(s_{21} + 2s_{22})] \quad (15)$$

with

$$\begin{aligned} c_1 &= 8w_2^{NN}/(8w_2^{NN} + 2w_2^{NNN}) & c_2 &= 2w_2^{NNN}/(8w_2^{NN} + 2w_2^{NNN}) \\ s_{11} &= [t_{11}(1 - t_{22}) + t_{12}t_{21}]/D & s_{12} &= t_{12}/D \\ s_{21} &= t_{21}/D & s_{22} &= [t_{22}(1 - t_{11}) + t_{12}t_{21}]/D \end{aligned}$$

and

$$D = (1 - t_{11})(1 - t_{22}) - t_{12}t_{21}.$$

The probabilities p_{\pm}^{ij} are calculated by a Monte Carlo method. The impurity is placed in the origin, imagining that it just made a jump from position (1,1,1) or from (2,0,0). The first case is an NN jump (type 1); the second is an NNN jump (type 2).

To calculate t_{11} and t_{12} the vacancy starts a large number of times from (1,1,1) to make a random walk through the lattice. When it returns to the origin, the random walk is terminated. The number of times that the vacancy jumps back to the origin gives the probabilities p_{\pm}^{ij} : the jumps from (1,1,1), (1,-1,1), (1,1,-1) and (1,-1,-1) contribute to p_{-}^{11} ; the jumps from (-1,1,1), (-1,-1,1), (-1,1,-1) and (-1,-1,-1) contribute to p_{+}^{11} . The vacancy jumps from (2,0,0) and (-2,0,0) give the probabilities p_{-}^{12} and p_{+}^{12} . For the calculation of t_{21} and t_{22} the vacancy starts from (2,0,0).

Since there are four different jump frequencies, the vacancy has different jump probabilities from sites close to the origin. Therefore for each of those sites an array is formed with 14 jump probabilities w_i , i.e. eight NN and six NNN jumps. The sum of these probabilities forms an interval

$$\left[0, \sum_{i=1}^{14} w_i \right]$$

containing 14 subintervals of length w_i . For sites farther from the origin the interval is simply

$$[0, 8w_0^{NN} + 6w_0^{NNN}].$$

A random number is drawn within the interval. The subinterval in which it lies determines which jump will be made by the vacancy. The vacancies that arrive in a site in the plane $x = 0$ will contribute equally to p_{+}^{ij} and p_{-}^{ij} . Since t_{ij} is the difference between these probabilities, it is possible to reduce the computer calculating time by terminating the walk of these vacancies. For the same reason the walk of vacancies can be stopped if they are relatively far from the origin. It turned out that a distance of ten lattice parameters was 'far'.

4. Results

For the numerical calculations, $T_m = 3000$ K and thus $H_{0NN}^M = 1.5$ eV was used. ΔH_{NN}^M was varied in steps of 0.1 eV from -0.6 to +0.6 eV. For the mass ratios m_0/m_2 the values $\frac{1}{3}$, 1 and 3 were taken into account. The calculations of the jump frequency ratios were performed by use of $w_0^{NN} = 1$.

For each value of ΔH_{NN}^M and m_0/m_2 the impurity diffusion correlation factor f_2 was calculated from $T/T_m = 0.4$ to $T/T_m = 1$ in steps of 0.1. The vacancy made 90000 starts, from both (1,1,1) and (2,0,0), which gave statistical errors smaller than 0.002. The results are shown in figure 1. The size of the points is larger than their inaccuracy. To show the coherence of the points, datum points with the same value of ΔH_{NN}^M have been connected by straight lines.

For large negative values of ΔH_{NN}^M the impurity is relatively mobile so that the vacancy has a high probability of exchanging with it, resulting in a low value of f_2 . $\Delta H_{NN}^M = 0$ and $m_0/m_2 = 1$ corresponds to the case of self-diffusion. The results for this case agree well with those calculated with other methods [6].

5. Discussion

In the present model, some rough simplifications have been made in order to avoid assumptions of a special impurity diffusion model. First, differences in the migration entropies are neglected, i.e. $\Delta S^M = 0$. Secondly the binding energy ΔH_{IV}^B between the impurity and vacancy is considered to be zero. $\Delta H_{IV}^B = -\Delta H_{IV}^F$ can be deduced from the frequency ratio of associative and dissociative jumps of the impurity vacancy pair, w_4 and w_3 respectively, according to $w_4/w_3 = \exp(\Delta H_{IV}^B/kT)$. Thus, the assumption that all host atom jumps have the frequency w_0 leads to $\Delta H_{IV}^B = 0$.

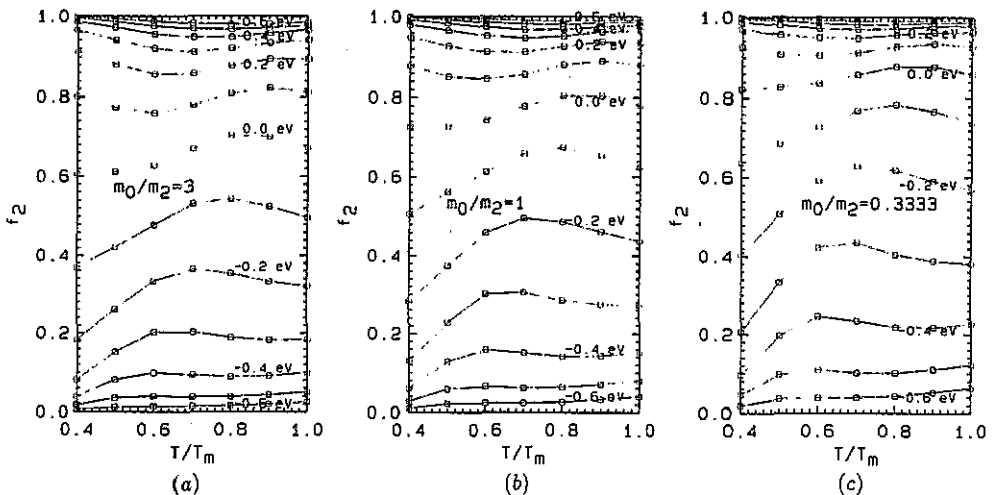


Figure 1. Correlation factor f_2 as a function of temperature for different values of ΔH_{NN}^M and m_0/m_2 : (a) $m_0/m_2 = 3$; (b) $m_0/m_2 = 1$; (c) $m_0/m_2 = \frac{1}{3}$. From top to bottom, ΔH_{NN}^M varies in steps of 0.1 eV from +0.6 to -0.6 eV.

Because of these simplifications it becomes obvious that a comparison between calculated correlation factors f_2 and experimentally determined isotope effects E_2 can only be qualitative. The comparison is further complicated by the fact that the kinetic energy factor ΔK in $E = \Delta K f$ is not well known.

The temperature function of E_2 for the impurity diffusion in group V and VI metals was only measured for Fe in V [14] and Mo and Cr in W [15]. Coleman *et al* [14] have investigated E_2 for Fe in V between 1300 and 2100 K, where E_2 decreases

from 0.7 to 0.3. However, recent measurements found the result that E_2 (1300 K) ≈ 0.32 [15]. Furthermore, the plots with $m_0/m_2 = 1$ and a small negative value of ΔH_{NN}^M (see figure 1) indicate that the measurements of Coleman *et al* are difficult to interpret.

For Cr in W, E_2 was measured between $0.57 T_m$ and $0.73 T_m$, resulting in a temperature-independent $E_2 = 0.13 \pm 0.02$ [15]. For Mo in W, E_2 increases from 0.16 to 0.21 between $0.52 T_m$ and $0.60 T_m$, while E_2 is about 0.32 ± 0.03 between $0.66 T_m$ and $0.73 T_m$ [15].

The experimental values of $\Delta Q = Q_2 - Q_0$ for the same temperature range are $\Delta Q(\text{Cr}) \approx -0.65$ eV and $\Delta Q(\text{Mo}) \approx -0.43$ eV [15]. When disregarding ΔH_{IV}^F and the temperature dependence of f_2 , ΔQ can be approximated by $\Delta Q_{NN} \approx \Delta H_{NN}^M$ and $\Delta Q_{NNN} \approx 2 \Delta H_{NN}^M$. For Cr in W, \bar{T} is about $\frac{2}{3} T_m$. Thus $\Delta Q(\bar{T})$ is between ΔH_{NN}^M and $2 \Delta H_{NN}^M$. With $\Delta Q \approx 1.5 \Delta H_{NN}^M$ the experimental values of ΔQ correspond to $\Delta H_{NN}^M(\text{Cr}) \approx -0.4$ eV and $\Delta H_{NN}^M(\text{Mo}) \approx -0.3$ eV. (In reality the amount of ΔH^M should be smaller, as $T_m(\text{W})/3000 \approx 1.2$ and as ΔH_{IV}^F is expected to be about $\frac{1}{6} \Delta H_{NN}^M$ [16].) With $m_0/m_2 \approx 0.3$ for Cr in W and $m_0/m_2 \approx 0.5$ for Mo in W the following temperature functions of f_2 can be derived from figure 1. For Cr in W f_2 is about 0.09 and almost temperature independent between $0.57 T_m$ and $0.73 T_m$. For Mo in W, f_2 increases from 0.19 to 0.25 between $0.52 T_m$ and $0.6 T_m$ and remains constant up to $0.7 T_m$. Qualitatively this is in agreement with the temperature behaviour of E_2 . In particular the temperature behaviour of f_2 for Cr in W supports the idea of the NN and NNN jump competition in group V and VI metals. In the case of exclusively NN monovacancy jumps, f_2 and thus E_2 should exhibit a strong increase with rising temperature (see e.g. [17]).

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