



Mechanisms of volume diffusion in metals near the Debye temperature

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HIGHLIGHTS

- A diffusion model is proposed at temperatures above ($T > T_D$) and below ($T < T_D$) the Debye temperature.
- At $T > T_D$ diffusion can be described in localized melting terms.
- At $T < T_D$ diffusion occurs as a result of fluctuation formation of a hollow diffusion corridor.
- The effect of reduced diffusion activation energy at low temperatures explained.

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ABSTRACT

The paper offers a phenomenological model of volume self-diffusion and interstitial diffusion at high ($T > T_D$) and low ($T < T_D$) temperatures (where T_D stands for the Debye temperature). Diffusion mechanisms at high and low temperatures were shown to differ greatly. Diffusion at high temperatures occurs as a result of fluctuations that can be described in the localized melting terms – 'liquid diffusion corridor' formation. At low temperatures when melting is difficult for a number of reasons, diffusion occurs through a 'hollow diffusion corridor' formed by fluctuation. Activation energy calculations for self-diffusion agree well with the $T > T_D$ experiment and show a dramatic increase in the activation energy at $T < T_D$. Interstitial diffusion activation energy calculated for BCC metals agrees well with the experiment of the whole temperature range and helps to explain why diffusion activation energy goes down at low temperatures.

1. Introduction

To date, experimental data on volume self-diffusion in various metal systems at high temperatures $T \geq 0.5T_m$ (T_m stands for material melting temperature) is extensive [1–11]. Experimental values of volume self-diffusion activation energy Q_{vs} that are generally obtained while studying diffusion permeability at $0.4–0.9T_m$ lie within the 18–20 kT_m range [1–4].

A vacancy mechanism is traditionally used to provide a theoretical description of volume self-diffusion and interstitial diffusion. According to the classical concept of diffusion mass transfer mechanisms observed in the crystal lattice, a diffusing atom shall jump into the vacancy formed. This concept brings the following volume self-diffusion coefficient expression [2–4]:

$$D_{vs} = D_{vs0} \exp(-(Q_{1s} + Q_{2s})/kT) \quad (1)$$

$$D_{vs0} = fz a^2 \nu_0 \exp((S_{1s} + S_{2s})/k) \quad (2)$$

where D_{vs0} is the pre-exponential factor; $f \sim 1$ is the correlation factor;

z is the coordination number; ν_0 is the frequency of atomic vibrations; Q_{1s} and S_{1s} are the energy and entropy of vacancy formation; Q_{2s} and S_{2s} are the energy and entropy of vacancy migration.

Unlike volume self-diffusion, interstitial diffusion in BCC metals is experimentally studied over a wider temperature range: apart from $T \geq 0.4–0.5T_m$ temperatures generally used to study diffusion, interstitial diffusion was studied at lower temperatures ($\sim 0.2T_m$). As a rule, indirect methods are applied to this end. One of those methods is based on studying principles of internal friction [12,13]. It is traditionally assumed that interstitial diffusion is the reason for two internal friction peaks in BCC metals: Snoek peak at temperatures close to $0.2T_m$ and Snoek-Koster peak at $0.3–0.4T_m$ temperatures [12,13]. Standard methods help to identify interstitial diffusion activation energy and in some cases, the concentration of impurity atoms in a solid solution [1–4]. However, it should be emphasized that the values of diffusion activation energies in atoms of one and the same interstitial impurity obtained for those temperature ranges differ greatly [13]. Thus, when studying Snoek relaxation for carbon atoms in iron [13], the values of interstitial diffusion activation energy were obtained within the range

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of $Q_{vi} \sim 5.1\text{--}5.5 kT_m$, where as the Snoek-Koster relaxation values stood higher at $Q_{vi} \sim 8\text{--}9 kT_m$.

An interstitial mechanism is used to provide a theoretical description for interstitial diffusion [2–4]. It is assumed that interstitial atoms need no vacancies for a diffusion jump as they spend energy only on migration from one interstitial space to another. The expression for interstitial impurity diffusion coefficient runs as follows:

$$D_{vi} = D_{0vi} \exp(-Q_{2i}/kT) \quad (3)$$

where D_{vi0} is the pre-exponential factor, Q_{2i} is the interstitial atom migration energy.

Rigorous calculations for vacancy formation energies Q_{1s} and migration energies Q_{2s} and Q_{2i} are rather complicated based on the initial principles and generally require adjustable ill-defined parameters [14]. Therefore there is a whole series of phenomenological models proposed to assess diffusion activation energy values. However, despite much effort current methods are still not efficient enough to calculate volume diffusion parameters in pure metals [14]. Paper [15] proposes a way to describe grain boundary self-diffusion at high temperatures in melting terms (see earlier papers [16,17]). Paper [15] shows that in order to ensure diffusion mass transfer in the grain boundary it is enough to melt a small portion (in size close to an inter-atomic distance) of the grain boundary through fluctuations and to transfer the atom in the melt. This model helped to achieve reasonable values of grain boundary self-diffusion activation energy for a wide range of pure metals.

The core idea of this paper is to apply the approach developed in paper [15] to describe volume self-diffusion and interstitial diffusion and based thereon to calculate volume self-diffusion activation energy in FCC and BCC pure metals and interstitial impurity diffusion energy in BCC metals.

2. Model of diffusion at high temperatures ($T > T_D$)

2.1. Self-diffusion

Similar to the way it was done in Ref. [15], let us assume that to ensure diffusion transfer of an atom in the crystal over a distance of the crystal lattice parameter, it is essential first to form a vacancy in the neighboring lattice site, second to melt a 'diffusion corridor' between a diffusing atom and a vacancy, and third to ensure migration of a diffusing atom along the resulting melt site. Diffusion activation energy value in this case may be presented as follows:

$$Q_{vs}^1 = Q_{1s} + Q_{ms} + Q_{Ls} \quad (4)$$

where Q_{1s} is the vacancy formation energy; Q_{ms} is the 'diffusion corridor' melting energy; Q_{Ls} is the melt diffusion activation energy. To determine Q_{1s} and Q_{Ls} values, table values provided in Refs. [14] and [15,18] respectively can be used. To assess Q_{ms} , following the approaches developed in Ref. [15], let us present the 'diffusion corridor' formation enthalpy as a combination of two members: bulk melting energy and surface energy:

$$Q_{ms} = \lambda \rho V^* + \gamma_{S/L} S^* \quad (5)$$

where λ is the specific heat of melting, ρ is the mass density, $\gamma_{S/L}$ is the liquid-crystal surface energy [15], V^* and S^* stand for the volume and area of the corridor surface.

Let us assume that the molten area is shaped like a cylinder with atomic radius r_s and length corresponding to interatomic distance b . In this case, $V^* = \pi r_s^2 b$ and $S^* = 2\pi(r_s^2 + r_s b)$. Plugging (5) in (4) with due regard to the above relations for V^* and S^* we shall get:

$$Q_{ms} = \pi r_s^2 b \lambda \rho + 2\pi(r_s^2 + r_s b) \gamma_{S/L} \quad (6)$$

Values of all the members constituting formula (4) that are calculated by formula (4), as well as volume diffusion activation energy values for a number of pure metals are presented in Tables 1 and 2

respectively. As shown in Table 2, experimental values of volume self-diffusion energy agree well with those calculated by formula (4).

2.2. Diffusion of interstitial atoms

We shall apply the above approach to describe volume interstitial diffusion. As in case of volume self-diffusion, a liquid 'diffusion corridor' is required with atomic radius r_i and length equal to the distance between neighboring interstitial sites. (This distance is generally similar to interatomic distance b). Interstitial diffusion activation energy Q_{vi}^I can be written as follows:

$$Q_{vi}^I = Q_{mi} + Q_{Li} + W_e \quad (7)$$

As above (see (5)), liquid 'diffusion corridor' formation energy Q_{mi} can be calculated by the following formula:

$$Q_{mi} = \pi r_i^2 b \lambda \rho + 2\pi(r_i^2 + r_i b) \gamma_{S/L} \quad (8)$$

where Q_{Li} is the interstitial diffusion activation energy in the melt; W_e is the elastic strain energy associated with dimensional discrepancy between an interstitial atom with radius r_i and an interstice with radius r_p where the atom is placed. At first approximation W_e is as follows:

$$W_e = K \left(\frac{\Delta V}{V} \right)_e^2 / 2 \quad (9)$$

where K is the bulk modulus of elasticity [18].

In turn, $(\Delta V/V)_e$ values are composed of three members: geometric contribution $(\Delta V/V)_g$, thermal expansion contribution $(\Delta V/V)_T$ and contribution related to volume jump during melting: $(\Delta V/V)_e = (\Delta V/V)_g - (\Delta V/V)_T - (\Delta V/V)_M$.

The geometric contribution $(\Delta V/V)_g$ is equal to the difference in volume between an octahedral (tetrahedral) interstice V_p and an interstitial atom in BCC lattice V_i at zero temperature $(\Delta V/V)_e = (V_p - V_i)/V_p = 1 - (r_i/r_p)^3$. The thermal expansion contribution at first approximation can be presented as follows: $(\Delta V/V)_T = N^* \beta \Delta T$, where β is the coefficient of volume expansion, N^* is the number of atoms surrounding the interstitial atom. The contribution $(\Delta V/V)_M$ related to volume jump during melting $\Delta V_m/V$ (for metals it is several percent $\Delta V_m/V \sim 4\text{--}6\%$ [15]) in the liquid 'diffusion corridor' equals $N^* \Delta V_m/V$. In this case the expression for $(\Delta V/V)_e$ runs as follows:

$$(\Delta V/V)_e = (\Delta V/V)_g - N^*(\beta \Delta T + \Delta V_m/V) \quad (10)$$

At $T = 0.5T_m$ and $N^* = 6$, $r_i = 0.77$ nm, $r_p = 0.66$ nm, $V_m = 0.05$, $\beta \Delta T \sim 0.05$ we get $(\Delta V/V)_e \sim 0.01$. Subject to such $(\Delta V/V)_e$, W_e calculated by formula (9) with due regard to (10) at $K\Omega/kT_m \sim 80$ [20] is very small $\sim 10^{-3} kT_m$. This means that during formation of a 'diffusion corridor' by melting, the contribution of elastic strain energy W_e to Q_{vi}^I may be neglected.

In this case the interstitial diffusion activation energy shall be determined by two members: energy required to create a 'diffusion corridor' Q_{mi} and interstitial migration activation energy in the melt Q_{Li} . Theoretical values of the diffusion activation energy calculated by formula (7) for interstitial atoms in various metal systems are presented in Tables 3 and 4. Tables show that they agree satisfactorily with experimental data on diffusion of impurity atoms at high temperature [1–4].

2.3. Discussions of the liquid diffusion corridor model

Let us discuss the conditions for applicability of the above model. In line with Lindemann model [26], the atom oscillation energy in the crystal atoms with m_a mass $W \sim m_a x^2 \nu^2 / 2$ shall reach some limit value W^* . As shown in Ref. [26], this is possible when the frequency of atom oscillations ν reaches its limit value – the Debye frequency ν_D , and the amplitude of oscillations x reaches some limit value x_{max} .

Chances to reach maximum frequency and amplitude of oscillations

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