Simulation of diffusion of hydrogen atoms in the lattice of tungsten
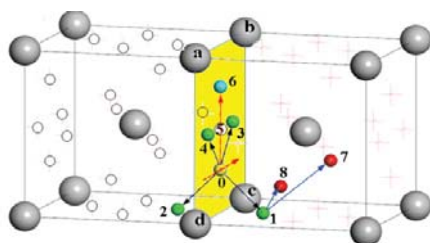
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Abstract. Results of DFT calculations of the activation energy for diffusion and vibrational spectra of interstitial hydrogen atoms in the lattice of tungsten are presented. The temperature dependences of the diffusion coefficient are calculated and compared with experimental data.

1. Introduction

For a long time, diffusion of hydrogen in tungsten has attracted interest for thermonuclear fusion. Early experimental works [1-5] were based on measurements of permeability and desorption and were carried out at high temperatures from 910 to 2500 K. The values of activation energies for diffusion obtained in those works were rather high from 0.86 to 1.8 eV; and only in the work of Frauenfelder [1] performed in the range of 1200-2000 K, a relatively low value of 0.4 eV was obtained. Experiments at low temperatures from 293 to 673 K were performed in later works [6-8] based on measurements of concentration profiles of radioactive tritium, and the activation energy for diffusion was 0.39 eV. Theoretical calculations based on first principles and performed at 0 K gave smaller values of the activation energy 0.19 eV [9] and 0.21 eV [10]. In a recent work [11], based also on first principles, two paths of transition between two interstitial tetrahedral sites were considered: a short jump between two closest tetrahedral sites, and a longer jump through an octahedral site. At the temperature of 0 K, the short jump had the activation energy of 0.22 eV, and the longer jump had the activation energy of 0.38 eV. To analyze the situation at higher temperatures, vibrations of tungsten atoms and thermal expansion of the lattice were taken into account. It was shown that activation energies for jumps increased from 0.18 eV to 0.40 eV for the short T-T jump and from 0.29 eV to 0.69 eV for the long T-O-T jump with increase of temperature from 300 K to 2500 K. Thus, the uncertainty in the activation energy for diffusion of hydrogen in tungsten remains rather large. This work is devoted to re-analysis of two paths of elementary jumps at 0 K and elevated temperatures basing on the DFT theory.

Figure1. Several positions of interstitial H atoms in the W unit cell. Positions 1-4 and 6-8 are tetrapores, position 5 is an octapore. Some short and long jumps between tetrahedral sites are shown.

Method

Optimization of the configuration of the system "W crystal – H atom" and calculations of

energies were performed in the DFT framework using super cells with periodic boundary conditions. In calculations, GGA approximation with PBE exchange-correlation functional and pseudopotential that keeps the norm was used. Cut-off of the kinetic energy was at ~720 eV. Positions of all atoms of the super cell were optimized to minimize the total energy of the cell. Self-consistency threshold of energy convergence was $5{\times}10^{-6}$ eV/atom during optimization of the system configurations.

In equilibrium, the hydrogen atom in the lattice of tungsten occupies a tetrapore, and figure 1 shows a few of them (positions 0-4 and 6-8). Also an octapore (position 5), where the energy of H atom is higher, is shown. Hydrogen atom can jump between two tetrapores in two ways: either directly between two nearest tetrapores (0-1 or 0-3, for example) or through an octapore (0-5-6, for example). Taking into account relaxation of the cell, the short distances 0-1, 0-2, 0-3, etc. are $\lambda_1 \approx a/\sqrt{8} \approx 1.13$ Å, and the long distances between 0-6, etc are $\lambda_2 \approx a/2 \approx$ of 1.6 Å. A hydrogen atom in position 0 can make 4 short jumps into sites 1-4, and 2 long jumps in sites 6 and 6* (symmetrically below position 0).

2. Energies and vibration frequencies at 0 K

The energy barriers for short and long jumps at 0 K are shown in figure 2. Calculations were performed using the linear and quadratic synchronous transition (LST/QST) with optimization. The short jumps 0-1, 0-3. etc need a smaller activation energy $\varepsilon_1 \approx 0.195$ eV, while the long jump 0-5-6 needs a higher activation energy $\varepsilon_2 \approx 0.37$ eV, which is almost equal to the value previously calculated in [12].
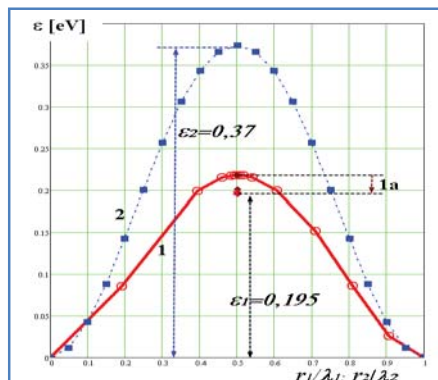
Figure 2. Total energy E_F along LST trajectories between two tetrapores: 1 – short path; 2 – long path, 1a – the energy within QST (one point at the top of the barrier).
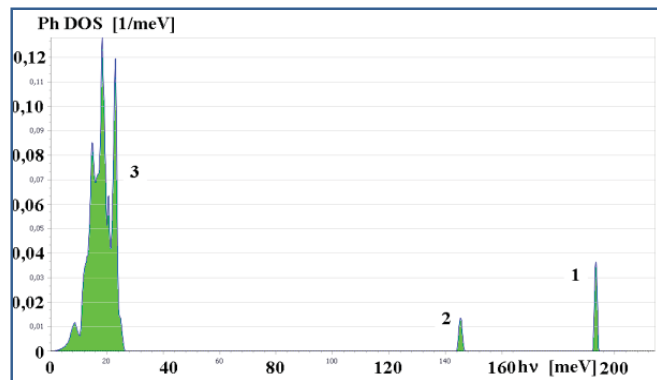
Figure 3. The density of phonon states (PhDOS) for W super cells with one interstitial H atom in an equilibrium tetrahedral site.

The phonon density of states (PhDOS) for W super cell with one H atom in the equilibrium interstitial tetrahedral site has several maxima (figure 3). Peak 1 is the oscillation of an atom in H modes with almost identical frequencies and amplitudes $h\nu_1 \approx 194$ meV (46.92 THz) and $h\nu_2 \approx 193.5$ meV (46.77 THz). The H atom oscillates along the line connecting nodes 0 and 6 that corresponds to the long jump through octapore. Peak 2 is the local vibration mode of the hydrogen atom with $h\nu_3 \approx 146$ meV (35.39 THz); and the direction of oscillations is perpendicular to the line 0-6 and coincides with none of short jump directions. There is also a set of oscillation modes of W atoms (group of peaks 3) in different directions with average frequency $h\nu_W \approx 16$ meV.

Calculations of PhDOS for the W supercell with one H atom on the top of the potential barrier for a short jump (0→1, e.g.) demonstrate three peaks associated with H vibration. Two local vibrations have real frequencies $h\nu^*_2 \approx 200$ meV (53.2 THz) and $h\nu^*_3 \approx 257$ meV (68.4 THz). There is also a mode of

H vibration with the imaginary frequency $h\nu*_1 \approx i \cdot 110$meV ($i \cdot 26.6$ THz). This indicates that the maximum of the energy in the short jump is a simple saddle point of the potential relief.

Calculations of the PhDOS for W super cell with one H atom in octapore, which is the top of the potential barrier for a long jump ($0 \rightarrow 5 \rightarrow 6$ e.g.), demonstrates one mode for the H atoms with the real frequency $h\nu**_3 \approx 290$ meV (70.1 THz) and two modes for the H atom with about equal imaginary frequencies $h\nu**_1 \approx h\nu**_2 \approx i \cdot 100$ meV ($i \cdot 24.2$ THz). Thus, the octapore (position 5) is a saddle point of the second order in the potential relief. It is surrounded by four equivalent tetrahedral sites and four valleys, and therefore has only one real frequency of H atom in this position, in contrast to the top of the barrier for a short jump.

Physically, this is due to the feature of the potential barrier vertex (points 5) for the long jump (0-6). This top is the saddle of the second order, as is surrounded by 4 equivalent positions (1,2,3,4), i.e. it has 4 valleys of the potential relief.

3. Diffusion coefficient

The diffusion coefficient D is defined as $D = D_0 \exp(-\Delta H_m / kT)$; $D_0 = \nu \cdot \lambda^2 \cdot \exp(-\Delta S_m / kT)$, where ΔH_m is the activation enthalpy for diffusion, ΔS_m is the activation entropy for diffusion. We will treat factor D_0 similar to [13,14]. In the theory of absolute rates of reactions [13], factor D_0 includes parameter $\Gamma_j(T)$, which is the ratio of the number of allowed states on the top of the reaction barrier to the number of possible states in the equilibrium state. This relationship can be represented through the number of states for a quantum oscillator. An expression for the frequency of jumps through a barrier ε was obtained in [14] basing on [13] using the approximation of a quantum harmonic oscillator with a spectrum, for which all states are allowed with $h\nu(n+1/2)$, ($n=0...\infty$).

Our calculations for the ground state of a quantum particle ($n=0$) give that $0.5 \cdot \sum_{i=1}^{3} h\nu_i = 267 meV$, i.e. the energy level of H atom in the potential well corresponding to the ground state is of about the same value as the height of the barrier. Similarly, zero vibrations change the energy state of the atom in saddle points on the top of the barriers, but to a smaller extent, since the number of real frequencies is smaller. In our case, $1/2 \cdot \sum_{i=1}^{2}(h\nu^*_i) \approx 225 meV$ for short jumps ($0 \rightarrow 1$) and $1/2 \cdot \sum_{i=1}^{1}(h\nu^{**}_i) \approx 145 meV$ for long jumps ($0 \rightarrow 6$). The correction to the zero oscillations of the H atom leads to effective decrease of the activation barriers by $\Delta_1(0 \rightarrow 1) = -0.042 eV$ and $\Delta_2(0 \rightarrow 6) = -0.122 eV$. As a result, one may expect that the effective activation barrier for the long jump 0-6 is reduced approximately down to $\varepsilon_{2eff} \approx \varepsilon_2 + \Delta_2 \approx 0.25 eV$ and that for the short jump 0-1 remains about the same $\varepsilon_{1eff} \approx \varepsilon_1 + \Delta_1 \approx 0.19 eV$.

In contrast to [14], we have taken into account only the ground state of the quantum oscillator ($n=0$) and the contribution of the first excited state ($n=1$), since the higher levels of vibrations of the oscillator will exceed the height of the barrier. Taking into account only the two states for the short jump (i.e., the mode $n= (000)$ and modes $(100), (010), (001)$), we have:

$$\Gamma_{(0-1)TST}(T) = \frac{kT}{h} \cdot \frac{e^{-\frac{(h\nu^*_1 + h\nu^*_2)}{2kT}}}{e^{-\frac{(h\nu_1 + h\nu_2 + h\nu_3)}{2kT}}} \cdot \frac{(1+e^{-h\nu^*_1/kT}) \cdot (1+e^{-h\nu^*_2/kT})}{(1+e^{-h\nu_1/kT}) \cdot (1+e^{-h\nu_2/kT}) \cdot (1+e^{-h\nu_3/kT})} \sim e^{-\frac{\Delta_1}{2kT}} \qquad (1)$$

A similar expression is obtained for the long jump, but only with one frequency:

$$\Gamma_{(1-6)TST}(T) = \frac{kT}{h} \cdot \frac{e^{-\frac{(h\nu^{**}_1)}{2kT}}}{e^{-\frac{(h\nu_1 + h\nu_2 + h\nu_3)}{2kT}}} \cdot \frac{(1+e^{-h\nu^{**}_1/kT})}{(1+e^{-h\nu_1/kT}) \cdot (1+e^{-h\nu_2/kT}) \cdot (1+e^{-h\nu_3/kT})} \sim e^{-\frac{\Delta_2}{2kT}} \qquad (2)$$

The diffusion coefficients for two types of jumps D were calculated using the standard expression

$$D_j(T) = \frac{1}{6}\lambda_i^2 \cdot n_j \cdot \Gamma_j(T) \cdot \exp(-\varepsilon_j / kT) \qquad (3)$$

where λ_j is the length of the jump ($\lambda_1 =1.13$ Å, $\lambda_2= 1.6$ Å); n_j is the number of nearest sites to jump. Activation energies were taken from DFT calculations $\varepsilon_1 \approx 0.195$ eV and $\varepsilon_2 \approx 0.37$ eV. Figure 4 shows the temperature dependencies of the diffusion coefficients calculated for the short and long jumps along with experimental data obtained in [1-3]. Results of calculations given in [11] are also shown for comparison. One can see that long jumps give a good agreement with experimental data obtained in [1] at high temperatures. Short jumps with smaller activation energies overestimate diffusivity. One must also remind that directions of vibrations discussed above are also in favor of long jumps.

The Arrhenius plots 1 and 2 in figure 4 are not exactly straight lines, nevertheless one may introduce a simple exponential approximation for the apparent diffusion coefficient $D(T) = 2.3\times10^{-7} \exp(-0.29/kT)$ m^{-2}s^{-1} shown by dashed line 4 in figure 4. The apparent activation energy 0.29 eV is less than $\varepsilon_2 = 0.37$ eV obtained in DFT. The reason is that parameter $\Gamma(T)$ depends on temperature, and vibrations reduce the effective activation energy roughly down to 0.25 eV for long jumps as it was discussed above. One must also mention that Fraunfelder's experimental data can be divided in two groups at 1250-1400 K and at 1400-2000 K with different inclinations, while the energy 0.39 eV is used as an average value for the whole range 1250-2000 K. Our apparent activation energy 0.29 eV describes the high temperature wing well. The low temperature wing can be affected by defects as it was discussed in [11,15].
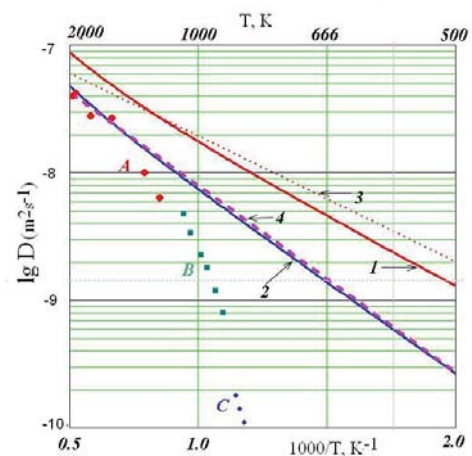

Figure 4. Temperature dependences of the diffusion coefficient D for the short (1) and long (2) jumps. Dotted line 3 – calculations [11]. Dashed line 4 is a simple exponential approximation. Experimental data: • - from [1]; ■ - from [2]; ♦ - from [3].

4. Conclusions

Potential energy of the W-H system with H atom jumping between two tetrahedral positions was calculated by DFT in the temperature range of 500-2000K for two types of jumps: a short jump between two nearest tetrahedral positions, and a longer jump through an intermediate octahedral position. The difference of energies in equilibrium tetrahedral position and in saddle points was $\varepsilon_1 \approx 0.197$ eV for the short jump and $\varepsilon_2 \approx 0.37$ eV for the long jump. Zero vibrations of atoms enhance the energy of the atom and reduce the effective activation energy down to roughly $\varepsilon_{1eff} \sim 0.19$ eV and $\varepsilon_{2eff} \sim 0.25$ eV, respectively. The diffusion coefficient calculated for long jumps is in a good agreement with experimental data of Fraunfelder in the range of 1400-2000 K and can be approximated by apparent diffusion coefficient $D(T) = 2.3\times10^{-7} \exp(-0.29/kT)$ m^{-2}s^{-1}. The experimental points in this temperature range can be described by smaller apparent activation energy than the activation energy 0.39 eV obtained in a wider temperature range. Short jumps overestimate diffusivity. Analyses of vibration directions is also in favor of long jumps, as vibrations of H atom take place in the directions of these jumps, while there are no vibrations in the directions of short jumps.

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