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Diffusion of helium in non-stoichiometric uranium dioxide

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ABSTRACT

Diffusion coefficients of helium in solid UO_{2+x} at high temperature and various stoichiometric compositions are evaluated by using molecular dynamics simulations based on a partly-ionic model in conjunction with a polaron 'Free Hopping Approximation' proposed earlier. The results are compared with existing experimental and simulation data. A strong dependence of the apparent diffusion activation energy on stoichiometry is found and the mechanisms of He migration in non-stoichiometric solid UO_{2+x} are discussed.

1. Introduction

The aim of the present work is to investigate by molecular dynamics (MD) the He diffusion mechanisms in non-stoichiometric uranium dioxide. It was intended to extend our previous MD simulation of defects formation and thermodynamic properties of non-stoichiometric uranium dioxide [1] based on a potential model proposed earlier [2].

The behaviour of helium in uranium dioxide has been extensively investigated since the middle of the 1960s, due to its potential effects on the nuclear fuel thermal and mechanical properties as well as on the spent fuel behaviour during long term storage and final disposal.

A number of measurements of He solubility and diffusion coefficients, D^{He}, were performed in a wide range of temperatures. First experimental data of Bostrom [3] ($T < 1000$ °C) appeared in 1957; further measurements at $T = 1200$ °C were published in 1964 by Rufeh et al. [4]. The results of Sung [5], published in 1967, are in a reasonable agreement with the diffusion data of Rufeh et al. [4].

Two experimental methods were generally adopted, respectively based on He infusion or He-ion implantation in the solid. Bostrom [3], Rufeh et al. [4] and Sung [5] used infusion to estimate the diffusion coefficients of helium in stoichiometric uranium dioxide, while Roudil et al. [6], Guilbert et al. [7], and Trocellier et al. [8] employed ion implantation.

The more recent paper of Ronchi and Hiernaut [9] is a bit detached from the others because these authors measured the diffusion coefficient of He atoms produced homogeneously in the bulk by α-decay reaction of a ^{238}Pu dopant, up to concentrations far above the saturation level, but with a confined lattice damage. This method gives a D^{He}, which is three to four orders of magnitude higher than that obtained in the other experiments (all performed at relatively low temperatures). The apparent diffusion activation energy of He recommended in Ref. [9], is about 2.6 eV, i.e. is in general agreement with the results of the other authors.

Measurements performed on UO_2 powders usually produce much higher He diffusion coefficients. Recent experimental data of Roudil et al. [6] cover the same temperature range $T < 1000$ °C, as the previous data of Bostrom [3], but provide D^{He} values which are one or two orders of magnitude higher.

Efforts have been made later to understand the reasons for these discrepancies and to investigate mechanisms of dissolution and migration of helium (as well as fission gases) in the nuclear fuels. Atomistic scale computer simulations based on different interatomic potential models represent one of the most promising ways to solve this problem. In 1965, Olander [10] was the first who attempted to calculate He solubility in stoichiometric UO_2. Grimes, Miller and Catlow in 1990 proposed an interatomic potential model and estimated the He solution and migration energies [11]. Efforts in this direction continued up to these days [12].

In the MD study of non-stoichiometric solids, a major additional problem appears, related to the simulation of the effect of electronic disorder, whose role on atomic diffusion has never been discussed so far. Electronic disorder is a local fluctuation of the dielectric constant, which may play an important role in migration processes occurring in ionic solids, in oxygen and helium diffusion particularly. This effect is caused by a fast (on a diffusion timescale) process of small-polarons 'hopping' over some energy barrier, enhancing all the transport processes in UO_{2+x} [13].

Recently we reported MD simulation experiments of solid non-stoichiometric uranium dioxide [1] based on a simple approximation for small-polaron hopping, called 'Free Hopping Approximation' (FHA). It was proposed in Ref. [1] to imitate the effect of electronic disorder in non-stoichiometric UO_{2+x} as described by an ionic model. Within the FHA, the hole (excess positive charge

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located on U^{5+} ions) in the hyper-stoichiometric dioxide (or excess electron of U^{3+} in the hypo-stoichiometric case) may freely jump from one lattice cation position to another. Using FHA we studied thermodynamic properties and defects formation in hyper-stoichiometric UO_{2+x} [1].

In the present paper we apply the same approach to study the behaviour of helium in non-stoichiometric uranium dioxide. Conventional MD computer simulations based on a Nosè–Hoover NPT ensemble were carried out using an extended, partly-ionic model [2] in conjunction with FHA, to study the behaviour of helium in UO_{2+x} for $-0.1 < x < 0.1$ and temperatures in the range 1800 K < T < 2700 K.

In Section 1, we describe the adopted potential model and provide basic results of static calculations of He incorporation energy and migration barriers. In Section 2, we report calculations of the He diffusion coefficient in stoichiometric UO_2. In Section 3, MD simulation of the He diffusion in non-stoichiometric UO_{2+x} solid are reported and the helium diffusion mechanisms are analyzed. The results finally are discussed and summarized in the last section.

2. Model of interaction in the He–UO_{2+x} system

The pair interaction potential of two particles in the He–U–O system consists of Coulomb, short-range and covalent bonding contributions:

$$\Phi_{\alpha\beta}(r) = \Phi^{(C)}_{\alpha\beta}(r) + \Phi^{(S)}_{\alpha\beta}(r) + \Phi^{(B)}_{\alpha\beta}(r). \tag{1}$$

The short-range interaction is described by Buckingham-type potential (α, β = He, O, U):

$$\Phi^{(S)}_{\alpha\beta}(r) = A_{\alpha\beta}\exp(-r/b_{\alpha\beta}) - C_{\alpha\beta}/r^6. \tag{2}$$

The electrostatic interaction of two ions of type α and type β is given by Coulomb's law:

$$\Phi^{(C)}_{\alpha\beta}(r) = \frac{q_\alpha q_\beta}{4\pi\varepsilon_0 r}, \tag{3}$$

where the total charges of the ions q_α and q_β are non-formal: $q_\alpha = Z^{\mathrm{eff}}_\alpha|e|$ and the effective charges $Z^{\mathrm{eff}}_\alpha = \zeta Z_\alpha$ are proportional to the respective formal charges ($Z_\alpha = +4$ for U^{4+} and $Z_\alpha = -2$ for O^{2-}). The ionicity ζ is considered as one of the free parameters of the model [2].

The additional energy of covalent bonding $\Phi^{(B)}_{\alpha\beta}(r)$ is attributed to U–O interactions and represented [2] by the Morse function:

$$\Phi^{(B)}_{\alpha\beta}(r) = D_{\alpha\beta}[\exp(-2\beta_{\alpha\beta}(r - r^*_{\alpha\beta})) - 2\exp(-\beta_{\alpha\beta}(r - r^*_{\alpha\beta}))]. \tag{4}$$

We applied the same parameters for O–O, U^{4+}–U^{4+} and O–U^{4+} interactions as we did in our previous work on stoichiometric UO_2 [2]. We retain the same potential function of Eq. (4) for the covalent O^{2-}–U^{5+} bonding, calibrated on the known lattice parameter of U_4O_9 in its β-phase, previously adopted in Ref. [1]. Information about the O^{2-}–U^{3+} interaction may be obtained from the enthalpy $\Delta H^{(\mathrm{dispr})}$ of disproportionation of the reaction $2U^{4+} \rightarrow U^{3+} + U^{5+}$, and experimental data on the oxygen potential $\Delta G^{(O)}(T)$ extrapolated at $T = 0$ K.

Regrettably, there exists a substantial discrepancy between the parameters obtained using different evaluations of $\Delta H^{(\mathrm{dispr})}$ and $\Delta G^{(O)}$(T), but all estimations show that the covalent O^{2-}–U^{3+} interaction is much weaker than the corresponding O^{2-}–U^{4+} interaction in stoichiometric UO_2. Hence, we neglected the covalent contribution for the O^{2-}–U^{3+} interaction. This assumption was confirmed by the comparison of the predicted and measured [14] lattice parameter of UO_{2+x} in the hypo-stoichiometric ($x < 0$) domain.

To estimate parameters of additional helium–oxygen and helium–uranium interactions we used the short-range potential for He–He, based on experiments of molecular beams scattering reported in Ref.[15] and adopted the simple combination rules:

$$b_{\alpha\beta} = (b_{\alpha\alpha} + b_{\beta\beta})/2; \quad A_{\alpha\beta} = \sqrt{A_{\alpha\alpha}A_{\beta\beta}}$$

for the unlike He–O and He–U^{4+} repulsion potential parameters $A_{\alpha\beta}$ and $b_{\alpha\beta}$ in Eq. (2).

Dispersion forces acting between He atoms are weak and have a small effect on the properties of helium both in the gaseous and in the condensed state. The dispersion well in the He–He potential is located at distances larger than 0.3 nm and has a depth of only approximately 0.003 eV [15].

At the same time, the dispersion effect due to the attraction of helium toward oxygen and uranium ions is much more pronounced, due to the polarization of the He atoms in the strong electrostatic field of the ions. Interstitial sites are believed to be the most stable positions for He atoms dissolved in perfect UO_2 [10–12]. The appropriateness of this assumption was repeatedly confirmed by *ab initio* calculations [16–18] as well as by experiments [19]. Therefore, He–O appears to be the most important interaction for predictions of the helium behaviour in UO_2 and, particularly, of the dispersion constant $C_{\mathrm{He-O}}$.

Olander in his earlier work [10] estimated $C_{\mathrm{He-O}}$. We adopted his recommended value combined with accepted parameters of He–O repulsion; using Olander [10] formula our model predicts the Henry constant a little higher than the existing experimental values obtained for single-crystals. Finally, we neglected the He–U dispersion forces and accepted Olander's dispersion constant $C_{\mathrm{He-O}}$ increased of 25% to reproduce recent experimental single-crystal solubility data of Blanpain et al. [20], which are in reasonable agreement with older measurements of Sung [5] on fused UO_2 single crystals of 10 μm size. In Fig. 1 we present a comparison of our calculations with the existing experimental data on He solubility.

To avoid the well-known unphysical behaviour of the resulting Buckingham-type interaction potentials at small r, all short-range $\Phi^{(S)}_{\alpha\beta}(r)$ potentials were replaced in the calculations by quadratic polynomials, having the same values and the first and second

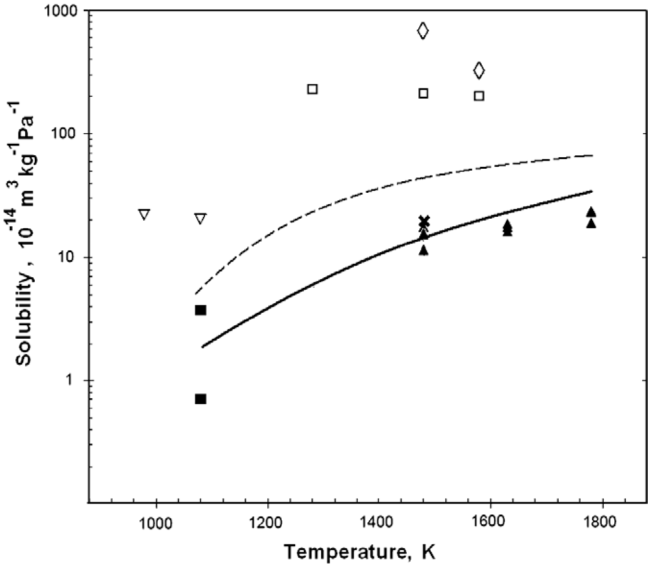

Fig. 1. Solubility of He in UO_2 as a function of temperature. Comparison with experimental data. Dashed line corresponds to the dispersion constant evaluated by Olander [10] and solid line to the 25% increased dispersion constant. Experimental data: single crystals (solid symbols): Sung[5] – triangles, Hasko and Szwarc [21] – squares, Blanpain et al. [20] – cross; powders (open symbols): Bostrom [3] – triangles, Rufeh et al. [4] – diamonds, Blanpain et al. [20] – squares.

derivatives at $r = 0.2$ nm, and smoothly increasing at shorter distances. The same He–U^{4+} potentials have been used for representing He–U^{3+} and He–U^{5+} interactions in non-stoichiometric UO_{2+x}. The whole set of potential parameters of a partly-ionic model for UO_2 is presented in Table 1.

Before MD simulation was carried out, we calculated the helium incorporation energies into a static UO_2 fluorite lattice with the experimental lattice parameter of 0.547 nm, for the interstitial sites and also for the oxygen and uranium vacancies, to assess the quality of our potential model. The He atom was placed into a given position (interstitial or vacancy), of a relaxed cell; then the cell was once more relaxed (maintaining the lattice parameter fixed) and the energy difference was estimated. All calculations were performed by using an MD cell containing 4000 uranium and 8000 oxygen ions ($10 \times 10 \times 10$ unit cells) with periodic boundaries. The results are presented in Table 2.

The energy required to incorporate He atoms into interstitial sites of a perfect UO_2 lattice $E_I(0)$, according to the present potential model, is about 0.45 eV, in qualitative agreement with the positive slope of the solubility versus temperature observed by Sung [5] in experiments on UO_2 single-crystals but in contrast to the *ab initio* predictions of Freyss et al.: −0.1 eV [18]. We predict the lowest incorporation energy at the uranium vacancy position $E_U(0) - E_I(0) = -0.5$ eV in a reasonable agreement with the recently published *ab initio* calculations of Yun et al. [17]: $E_U(0) - E_I(0) = -0.7$ eV. However, the predicted He incorporation energy at the oxygen vacancy position, $E_O(0)$, is somewhat lower than at the interstitial site ($E_O(0) - E_I(0) = -0.2$ eV), which is in contrast to both *ab initio* calculations of Yun et al.: +0.67 eV [17] and those of Freyss et al.: +2.5 eV [18]. One could object that *ab initio* calculations [16–18] were performed with different approximations and adopting very small boxes. It is, however, uncertain whether the latter conditions might explain this disagreement, since additional investigations reveal that in our calculations the sensitivity of this gap to the box size is rather small (a few percents only).

We also assessed the energy profiles of He atoms displaced in the UO_2 lattice from one interstitial site into another, and from an oxygen (uranium) vacancy into the neighbouring interstitial site. A single He atom, placed near to the central interstitial position (in the $10 \times 10 \times 10$ unit cell), was first displaced from this position along a certain crystallographic direction. The cell was then relaxed at a fixed distance of this atom from its initial position by varying the direction of its radial-vector and the positions of all other atoms (except those on the cell boundary). Finally the energy difference relative to the initial position was computed for a set of such displacements ending in the neighbouring interstitial site or oxygen or uranium vacancy.

The interstitial-to-interstitial crystallographic direction [1 1 0] is believed to be a favourite elementary migration path in stoichiometric UO_2. According to our calculations, this path is associated with a rather high ∼2.6 eV barrier (in agreement with *ab initio* calculations of Yun et al.: 2.79 eV [17] and estimations of Govers et al. [12] based on RFO and nudged elastic band calculations methods). Migration via oxygen vacancy along the [1 1 1] direction has a remarkably lower (∼0.5 eV) barrier (close to the *ab initio* 0.41 eV [17] and Grimes's et al. 0.38 eV [11] predictions). Note that in stoichiometric dioxide an additional (∼ 5 eV) formation energy of an oxygen Frenkel pair (OFP) is required. However, this second path represents an important alternative for the helium migration path in non-stoichiometric dioxide containing intrinsic oxygen vacancies, and is effective both in the hypo- and the hyper-stoichiometric domains. Formation of uranium vacancies gives rise to a further migration path for He with an even lower barrier ∼0.4 eV (or 0.79 eV according to Ref. [17]), but the formation energy of uranium Frenkel pair (UFP) is very high (∼14 eV).

In Fig. 2 we compare the adopted He–O interaction potential (the most important in the description of He solubility and diffusion), with the Lennard-Jones potential proposed by Grimes et al.

Table 1
Parameters of partly ionic potential model of the He + UO_{2+x} system (energy in eV; distance in 10^{-10} m, ionicity $\zeta = 0.5552$).

Ion pairs α–β	$A_{\alpha\beta}$	$b_{\alpha\beta}$	$C_{\alpha\beta}$	$D_{\alpha\beta}$	$\beta_{\alpha\beta}$	$r^*_{\alpha\beta}$
O–O	883.12	0.3422	3.996	–	–	–
U–U	187.03	0.3422	0	–	–	–
U^{3+}–O	432.18	0.3422	0	0	–	–
U^{4+}–O	432.18[a]	0.3422	0	0.5055[a]	1.864	2.378
U^{5+}–O	432.18	0.3422	0	0.849	1.864	2.1
He–He	169.0	0.257	0.580	–	–	–
He–U	177.8	0.300	–	–	–	–
He–O	386.3	0.300	15.786	–	–	–

[a] In Table 1 of the original paper [2] these values were incorrect. Authors are grateful to all who pointed our attention to these misprints.

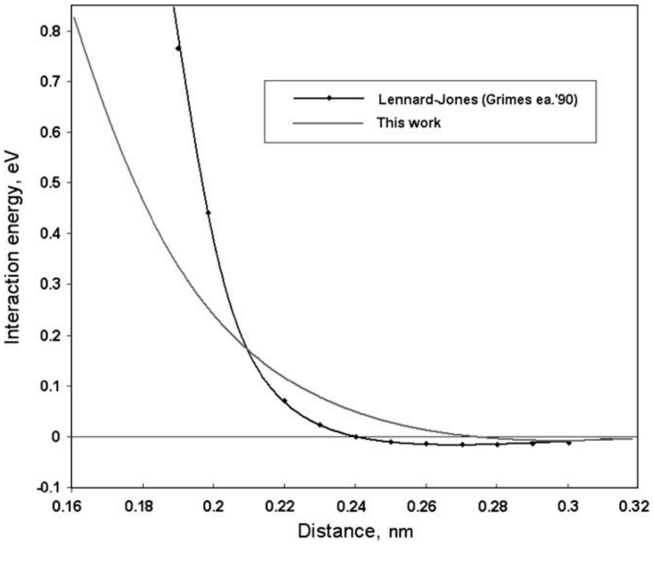

Fig. 2. Comparison of the adopted He–O short-range interaction potential with the Lennard-Jones potential proposed by Grimes et al. [11] and used in MD simulation of Govers [12].

Table 2
Calculated energies of defect formation, He incorporation energies $E_I(0)$, $E_O(0)$ and $E_U(0)$ and static barriers (eV) for displacements of He atoms from different initial positions into nearest interstitial site in a relaxing MD cell containing 4000 uranium and 8000 oxygen ions with periodic boundaries. Comparison with results[a] of Grimes et al. [11] and Govers [12].

Initial He position	Defect formation energy	Incorporation energy	Direction	This work	Static barrier	
					Ref. [11]	Ref. [12]
Interstitial site	–	0.45	[1 1 0]	2.56	3.80	2.3
Oxygen vacancy (OFP)	5.1	0.30	[1 1 1]	0.54	0.38	0.5
Uranium vacancy (UFP)	14	−0.02	[1 0 0]	0.43	0.24	0.2

[a] Govers [12] used the same Lennard-Jones potential of Grimes et al. [11] but applied a different technique to estimate the migration barrier.

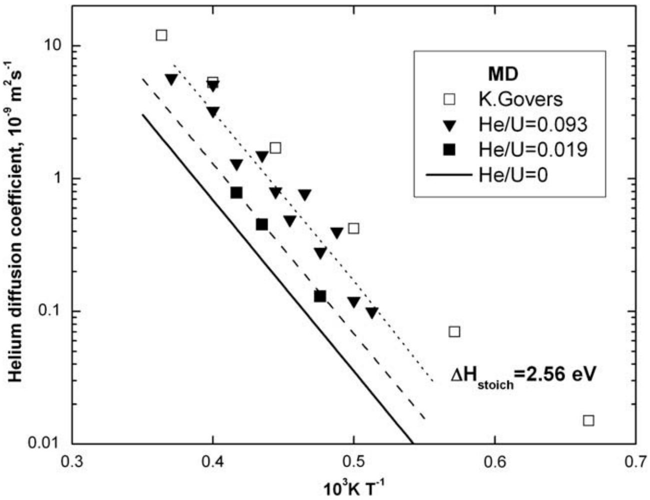

Fig. 3. Diffusion coefficient of He in stoichiometric UO_2. Comparison of our simulations with different helium concentrations (He/U = 0.093 and 0.019) with MD data of Govers [12] (open squares). The solid line represents extrapolation of our data on zero He concentration.

[11] and used in recent calculations by Govers et al. [12]. As one can see, Grimes's potential is much steeper than that we adopted. The enormous rigidity of Lennard-Jones (12-6) potentials at short distances is well known, and contradicts the results of experiments on scattering of molecular beams as well as the behaviour of *ab initio* based potentials [15]. This rigidity may lead to a very strong He–O repulsion at short distances and remarkably higher migration barrier (see Table 2). At He–O distances of 0.22–0.24 nm, which are typical for positions of He atom in an interstitial site, the helium–oxygen repulsion forces predicted by both models are similar. Hence, this feature appears crucial only for solubility predictions, whilst migration barriers and diffusion coefficients of He in stoichiometric UO_2 obtained in our MD simulation do not differ very much from those calculated by Govers et al. [12] (see Fig. 3).

3. Helium diffusion in stoichiometric UO_2

At the start of a MD simulation, a number of He atoms was randomly distributed in the cell near the centres of interstitial sites, and, after a suitable equilibration time, the He diffusion coefficient, as well as the equilibrium lattice parameters and other thermodynamic properties such as thermal expansion, compressibility and heat capacity were computed as described in Ref. [2]. The simulation parameters are as follows: timestep = 1 fs, total time of the MD run = 20–200 ps, depending on the box size, temperature and the number of He atoms. FHA hopping was performed every 20 fs as described in Ref. [1]. The diffusion coefficient of He, D^{He}, was found directly by sampling the slope of the mean squared displacements computed every 20 fs [1].

Even at high temperatures, helium is poorly thermodynamically soluble in UO_2. However, due to the slow He diffusion, simulations in the stoichiometric case are feasible with desktop computers only for substantial He concentrations and in a high-temperature domain ($T > 1500$ K). At relatively low temperatures ($T < 1500$ K), especially for small concentrations of He atoms, the simulation time needed to achieve a reasonable accuracy becomes impracticable. Hence, in such simulations of stoichiometric dioxide, the concentrations of He atoms cannot be kept as low as they are in reality at any cell size.

Consequently, we adopted the following approach. MD simulations were performed at two He concentrations, all of them much higher than those at the thermodynamic equilibrium. We then applied a linear extrapolation to zero He-concentration. In practice, diffusion coefficients of He in stoichiometric UO_2 were computed for the two concentrations He/U = 9.3 at.% (108 U-ions + 216 O-ions + 10He: $3 \times 3 \times 3$ unit cell), and He/U = 1.9 at.% (864 U-ions + 1728 O-ions + 16 He: $6 \times 6 \times 6$ unit cell) and extrapolated to He/U = 0.

Results are presented and compared with MD simulation data of Govers et al. [12] in Fig. 3. The increase of the He diffusion coefficient with increasing concentration of He was found to be essential, but the apparent diffusion activation energy (AAE) ΔH is almost independent of the He concentration. Extrapolating to zero concentration we obtained $\Delta H \approx 2.56$ eV in a good agreement with the estimated height of the barrier of the migration path along the [1 1 0] direction between two neighbouring interstitial sites. In this sense our results are similar to those published by other researchers. Note that the He diffusion coefficient calculated by Govers et al. [12] in the interval (1500 K < T < 2750 K) is somewhat higher than our predictions but has almost the same ΔH.

The remarkable raise of the diffusion rate with increasing concentration of helium is mainly due to the increase of the equilibrium lattice parameter (swelling). At $T = 0$ this effect was estimated in Ref. [17]. The computed lattice parameter actually increases linearly with the concentration of helium as it does with temperature.

Summarizing a number of simulations performed, we recommend the following approximate relation:

$$\Delta a = 6 \times 10^{-8} T \cdot (\mathrm{He/U}), \qquad (5)$$

where Δa is the increase of the lattice parameter (in nm) with increasing temperature, T in K, (He/U) ratio in at.%. This equation can be used to estimate the thermal effect of swelling due to presence of He at temperatures 1800 < T < 2500 K.

Furthermore, we computed the He diffusion coefficient in the liquid phase at T = 8000 K and compared it with the results of MD simulation of Govers [12]. Our simulation (at a pressure $P = 10^5$ Pa) predicts D^{He} something higher (4×10^{-7} m^2 s^{-1}) than that obtained by Govers (1.3×10^{-7} m^2 s^{-1}).

In Fig. 4 the predicted He diffusion coefficient (solid line) is compared with simulations of Govers et al. [12] and existing experimental data. Our estimations are in excellent agreement (both in magnitude and AAE) with the measurements of Ronchi and Hiernaut [9] on ^{238}Pu-doped UO_2.

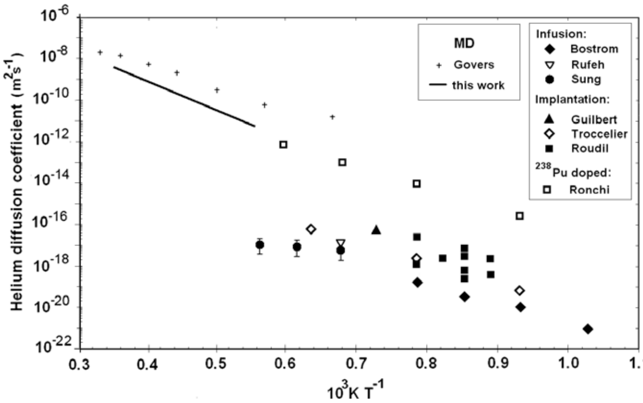

Fig. 4. Diffusion coefficient of He in stoichiometric dioxide. Comparison of our results and MD simulations of Govers [12] (crosses) with existing experimental data [3–9].

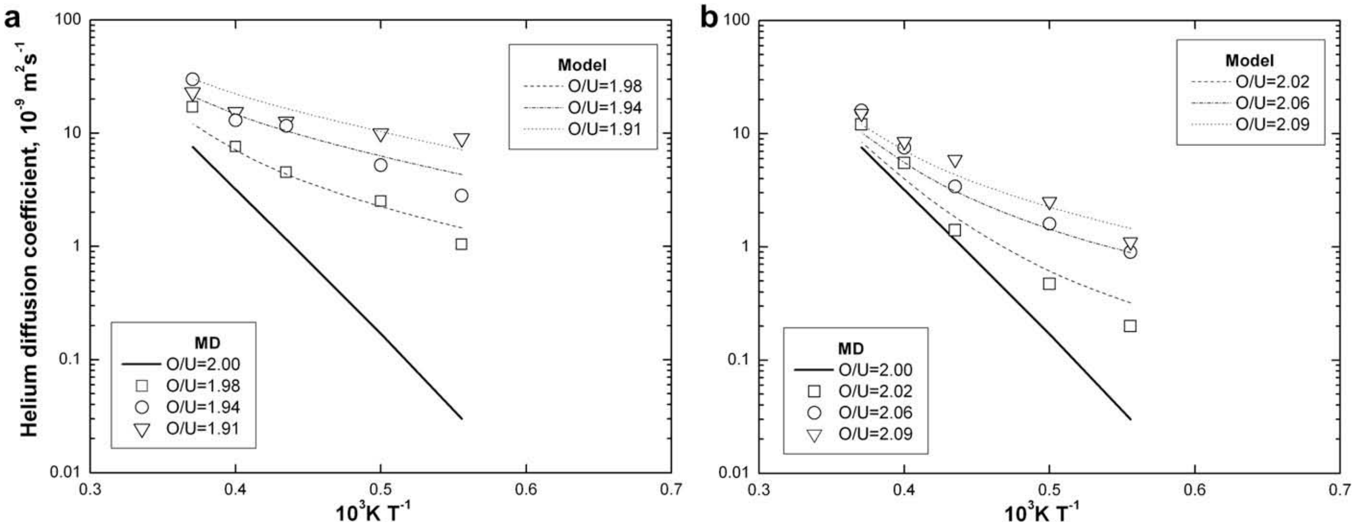

Fig. 5. He diffusion coefficients computed at high concentration of He atoms (He/U = 0.093): 108 U + 216 O (3 × 3 × 3 unit cells) + 10 He in hypo-stoichiometric (a) and hyper-stoichiometric (b) uranium dioxide. The solid line corresponds to the dotted line in Fig. 3 (stoichiometric UO_2 with the same He/U ratio), dotted and dashed lines represent empirical Eq. (6).

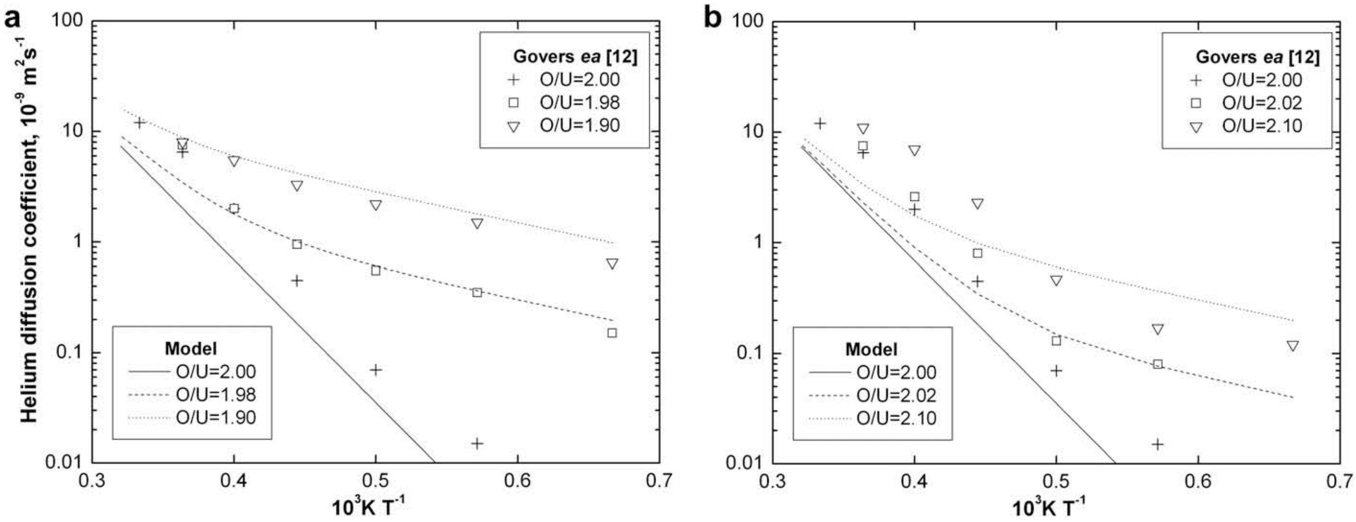

Fig. 6. Comparison of MD results of Govers [12] (based on Basak potential) in hypo-stoichiometric (a) and hyper-stoichiometric (b) uranium dioxide with the proposed empirical formula Eq. (6). The solid line (stoichiometric UO_2) corresponds to the solid line in Fig. 3 (He/U = 0).

4. Mechanisms of helium diffusion in UO_{2+x}

According to our static calculations presented in Table 2, in non-stoichiometric and defective uranium dioxide, positions exist, which are energetically more favourable for He atoms than the lattice interstitial sites: e.g., oxygen vacancy with He incorporation energy $E_O(0)$ of 0.3 eV and uranium vacancy ($E_U(0) \sim 0$). Both positions[1] correspond to lower static lattice energy but, due to competition with diffusing oxygen and uranium ions, the relative population of interstitial and vacancy sites occupied by He at high temperatures is not so obvious. MD simulation may provide important information about the role of defects in the dissolution and about the mechanisms of He diffusion in non-stoichiometric dioxide.

We studied non-stoichiometry effects on helium diffusion at five temperatures (1800, 2000, 2300, 2500 and 2700 K) and six values of the O/U ratio: three in the hyper-stoichiometric domain O/U = 2.02, 2.06, 2.09 and three in the hypo-stoichiometric region O/U = 1.91, 1.94, 1.98. We used different cell sized starting from 3 × 3 × 3 up to 10 × 10 × 10 (as used in our static calculations). The sensitivity study performed shows that at $T > 1800$ K the adopted 3 × 3 × 3 cell leads to a reasonable accuracy (~20%) of the calculated diffusion coefficient. Furthermore, at high temperatures it simultaneously allows avoiding the unphysical interaction of cuboctahedral clusters and entails an acceptable simulation time.

According to our calculations, even small deviations from stoichiometry significantly accelerate He diffusion. This effect is related to polaron hopping, and becomes more noticeable with decreasing temperature. The increase of He diffusion with deviations from stoichiometry is remarkably more pronounced in the hypo-stoichiometric domain. It is clearly seen from comparison of simulation data presented in Figs. 5 and 6. For instance at 1800 K and O/U = 1.91 ($x = -0.09$) D^{He} is about 300 times higher than in stoichiometric dioxide but at O/U = 2.09 ($x = +0.09$) this

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[1] Almost the same value of incorporation energy corresponds to the He atom inside the Schottky trivacancy.

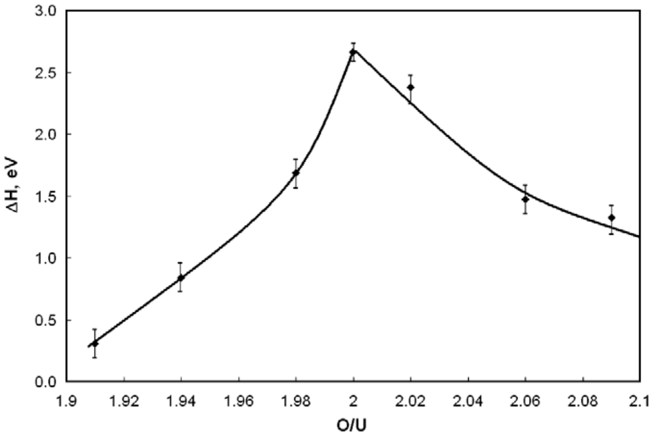

Fig. 7. The estimated apparent activation energy of He diffusion in UO_{2+x} has a maximum for stoichiometric UO_2.

factor is approximately 40. To estimate the effect of polaron hopping, we performed the following experiment. After the equilibrium was established, polaron hopping was 'switched off', and we observed a sharp drop of D^{He}. At $T = 1800$ K in hyper-stoichiometric uranium dioxide (O/U = 2.09) D^{He} decreases by a factor of 12, whilst under hypo-stoichiometric conditions (O/U = 1.94) it decreases by a factor of 25. The comparison of our results with MD simulation of Govers et al. [12] (see Fig. 6), also confirms the effect of polaron hopping on He diffusion both in hypo-stoichiometric and hyper-stoichiometric uranium dioxide. According to calculations of Govers (no hopping, Basak potentials), the effect of non-stoichiometry on D^{He} is remarkably smaller than in this work (about 100 times at O/U = 1.9 and approximately 10 times at O/U = 2.1 at the same temperature).

The frequency of the FHA also may have an influence on the oxygen and helium diffusion. We performed additional simulations and a sensitivity study at a much higher FHA frequency (one attempt of hopping every 2 fs instead of 20 fs). No significant effect on diffusion rate was found.

The apparent Arrhenius activation energy of diffusion determined by the slope of log D^{He} plotted against reciprocal temperature, decreases with increasing deviation from stoichiometry and decrease of temperature. The AAE values, determined at relatively low temperatures from data presented in Fig. 5, are plotted in Fig. 7. In the hyper-stoichiometric solid at O/U = 2.09 it is about 1.3 eV, in hypo-stoichiometric system at O/U = 1.91 it becomes even less than 1.0 eV.

The explanation of this change in AAE of helium diffusion requires a detailed analysis of the possible configurations of He atoms and their migration events during MD simulation of non-stoichiometric dioxide. Our computer code was additionally modified to allow continuous monitoring of He atoms positions and their movements over all vacant and occupied lattice and interstitial sites as well as visual analysis using the *Jmol* software [22] as described in Ref. [1]. To find out the reason for such behaviour of the AAE in non-stoichiometric dioxide, we analyzed site-to-site trajectories of He atoms during MD simulation runs. We found that the additional He diffusion mechanism dominating in non-stoichiometric UO_{2+x} is a two-step interstitial-to-interstitial migration path via intermediate oxygen vacancy along the crystallographic direction [1 1 1] (Fig. 8). This is also the most significant additional channel of helium migration in high-temperature stoichiometric dioxide. The higher the concentration of oxygen vacancies, the more this additional channel of the indirect [1 1 1] – migration contributes to the overall helium diffusion rate.

The 'direct' migration along [1 1 0] is associated with a high (~2.6 eV) barrier, the indirect [1 1 1] interstitial-vacancy-interstitial path has a barrier of only ~0.5 eV (see Table 2) and the incorporation energy in an oxygen vacancy (0.3 eV) is less than in an interstitial site.

High concentrations of oxygen vacancies exist not only in the hypo-stoichiometric but also in the hyper-stoichiometric domain, due to formation of OFP (at high temperatures) or cuboctahedral pentamers [1] at lower temperatures. At small deviations from stoichiometry the contribution of such additional diffusion channels should be proportional to the concentration of oxygen vacancies.

Accounting for these two different mechanisms of diffusion, we attempted to fit our simulation data using a simple model equation:

$$D^{He} = D_0 + A_1 \cdot |x| \cdot exp(-\Delta H_1/kT), \qquad (6)$$

where $D_0 = A_0 \cdot \exp(-\Delta H_0/kT)$ is the contribution from 'direct' interstitial-to-interstitial mechanism with activation energy $\Delta H_0 = 2.56$ eV and the second term corresponds to the additional (via oxygen-vacancy) migration mechanism with $\Delta H_1 = 0.54$ eV (value estimated over the migration path).

Comparison of the computed He diffusion coefficients at high concentration of helium (He/U = 0.093) with model Eq. (6) in non-hypo-stoichiometric solid is shown in Fig. 5. The solid line represents the diffusion coefficient at the stoichiometric value and the dotted and dashed lines represent the diffusion coefficient D^{He} calculated according to the model of Eq. (6). The pre-exponential factors A_0 and A_1 depend on the concentration of He atoms and the magnitude of A_1 is different in hypo- and hyper-stoichiometric domains. According to our estimations, at He/U → 0 are:

$$A_0 = 1.0 \times 10^{-4}\ \mathrm{m^2\ s^{-1}}, \quad A_1^{(\mathrm{hypo})} = 6.4 \times 10^{-7}\ \mathrm{m^2\ s^{-1}}, \quad \text{and} \quad A_1^{(\mathrm{hyper})} = 1.3 \times 10^{-7}\ \mathrm{m^2\ s^{-1}}.$$

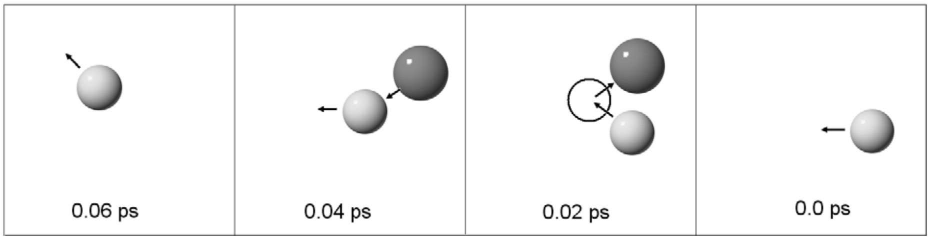

Fig. 8. Vacancy-assisted mechanism of an He atom (light gray sphere) diffusion. The dark sphere represents an oxygen ion displaced into an interstitial position and forming instantaneously a Frenkel pair with a vacancy (open circle). The MD simulation refers to stoichiometric UO_2 at $T = 2300$ K. Uranium and oxygen ions in their lattice positions are not shown for the sake of clarity.

5. Conclusions

The diffusion of He in UO_{2+x} was investigated with a model of small-polaron hopping, called 'Free Hopping Approximation' (FHA), proposed and tested in our previous paper [1]. FHA imitates polaron hopping by a fast exchange of the instant positions of the excess charge localized on U^{3+} ($x < 0$) or U^{5+} ($x > 0$) ions and has an important effect on the stability of different types of clusters formed in the hyper-stoichiometric domain [1].

Our results for both hyper-stoichiometry and hypo-stoichiometry are in reasonable agreement with those reported by Govers et al. [12], especially at higher deviations from stoichiometry. His calculations have been performed in the frame of a conventional MD simulation, i.e. without oxygen vacancy (interstitial) charge-compensation, and, consequently, without polaron hopping contribution, but cover a broader temperature range down to 1000 K.

The results of Govers et al. [12] in hypo-stoichiometry shown in Fig. 6a are in a good agreement with the model proposed and indicate an AAE of 0.5 eV, similar to the value found in this work.

In hyper-stoichiometry our results at high temperature (Fig. 6b) are somewhat different, as only "intrinsic" diffusion has been observed. The discrepancy could be due to the different types of clusters formed when conventional MD is used (i.e., without charge equilibration, what, however, might be acceptable at relatively low temperatures) and to the FHA technique [1] used in this work.

At relatively low temperatures we observed here very long (more than 100 ps) equilibration periods due to formation of isolated cub-octahedral clusters. To estimate reliable values of the He diffusion coefficient, one needs here a simulation time of about 200 ps.

An atomistic study of helium behaviour in non-stoichiometric uranium dioxide under high-temperature conditions requires explicit accounting for the local charge distribution created around oxygen vacancies or interstitials. In this work we found that polaron hopping strongly enhances the He diffusion coefficient.

MD simulations of UO_{2+x} doped with He, performed in this work in a wide range of temperatures and deviations from the stoichiometry, reveal a decrease of the apparent activation energy of helium diffusion both in the hypo- and hyper-stoichiometric domains (Fig. 7). In the hypo-stoichiometric domain, at relatively low temperatures, this decrease is almost proportional to the concentration of vacancies. In the hyper-stoichiometric domain the AAE decreases too, but the decrease is remarkably weaker. There are two reasons for this behaviour. First, the concentration of oxygen vacancies here is lower. Secondly, helium diffusion via interstitial sites is hindered because more interstitial sites are occupied by extra- and displaced oxygen ions.

The analysis of He migration events reveals additional details of 'direct' and vacancy-assisted migration mechanisms. 'Direct' [1 1 0]-migration between two interstitial positions occurs actually via occupied oxygen or uranium sites. It is the main diffusion mechanism at stoichiometry and relatively low temperatures. At higher temperatures the migration mechanism via vacancies (created by the formation of an intrinsic FPs or displacing of lattice ions into interstitial positions by diffusing He atoms) becomes more important.

In Fig. 8 we present a few trajectory fragments of one He atom, as visualized by *Jmol* [22], illustrating this indirect (O-vacancy assisted) interstitial-to-interstitial path. These events consist of jumps lasting less than 0.1 ps and occurring very rarely, especially at low temperatures and small deviations from stoichiometry. We found that at 2300 K about 10% of interstitial-to-interstitial jumps of He atoms in UO_2 were assisted by oxygen vacancies. At 2500 K this portion reaches 20% and its contribution becomes comparable to the 'direct' [1 1 0]-migration near the temperature of the premelting transition (~2700 K). At high temperatures we observed migration events combining these two mechanisms.

Vacancy-assisted mechanism is predominant under hypo-stoichiometric conditions especially at lower temperatures and is essential at hyper-stoichiometry. According to our estimations at rather low temperature ($T = 1800$ K) the contribution of the vacancy-assisted mechanism at O/U = 1.91 is roughly 60%, and is about 35% at O/U = 2.09. At higher hypo-stoichiometry a part of vacancy-assisted migration events appear via transient uranium vacancies, produced by uranium ions displaced to (unstable) neighbouring interstitial positions.

Starting from this observations, we proposed the simple formula Eq. (6), based on our MD simulation data allowing to estimate the He diffusion coefficient in UO_{2+x} in the studied temperature $1800\text{ K} < T < 2700\text{ K}$ and stoichiometry intervals ($-0.1 < x < 0.1$).

In conclusion, we note that He diffusion in the bulk of single-crystalline grains studied here is crucial for many processes in nuclear fuels where helium is produced by α-decay reactions. Among them the basic ones are lattice saturation and subsequent contribution to the formation of gas bubbles in conjunction with fission gas in irradiated fuel. On the other hand, the *macroscopic* helium release rate in polycrystalline fuels depends on the ceramographic structure of the pellets, where grain boundary diffusion plays an essential role [23]. MD simulation of polycrystalline UO_2 with He atoms enabled to migrate along grain boundary networks have been started. Preliminary results indicate that the grain boundaries diffusion has an apparent activation energy of only ~0.1 eV. Yet, the problems related to MD simulation of these and other types of structural defects affecting the microscopic and macroscopic diffusion rates of helium are far beyond the scope of this paper and will be discussed in more detail elsewhere.

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