Journal of Nuclear Materials 389 (2009) 119–126

Contents lists available at ScienceDirect

Journal of Nuclear Materials

journal homepage: www.elsevier.com/locate/jnucmat

Computer simulation of defects formation and equilibrium in non-stoichiometric uranium dioxide

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ABSTRACT

Formation and stability of different types of clusters in hyperstoichiometric UO_{2+x}, including Willis's 2:2:2 interstitial dimers as well as cuboctahedral tetra- and pentamers are investigated under static and dynamic conditions based on a partly-ionic model. A 'Free Hopping Approximation' for small polarons is proposed and implemented in a molecular dynamic simulation computer code. Lattice parameter and other equilibrium properties of UO_{2+x} are calculated and compared with existing experimental data in a wide range of temperature and stoichiometry.

1. Introduction

The uranium–oxygen system in the solid phase has been extensively studied because of its importance in fabricating and operating uranium dioxide, the most common nuclear reactor fuel during the past fifty years. A number of solid uranium oxides are known to have the ideal compositions UO_2, U_4O_9, U_3O_7, U_2O_5, U_3O_8, and UO_3 at room temperature and atmospheric pressure [5]. There exist a few representative database collections and empirical correlations of this oxide system, elaborated in USA [1,2] and Europe [3,4], which consider not only thermodynamic data but also phase equilibrium information. In these collections attention is particularly dedicated to the stoichiometric and non-stoichiometric dioxide (urania), which represents the typical chemical form of the sintered nuclear fuel pellets. Nonetheless, several details of the structure and phase diagram of urania still remain obscure. The oxygen in UO_{2+x} is known to occupy different types of site. Excess oxygen ions are located in interstitial sites near the ideal tetrahedral positions without significantly affecting the cation positions. Extra-oxygen ions may be considered as randomly distributed near interstitial sites only for values of x close to zero. At higher hyperstoichiometry levels, experimental evidence of extra-oxygen cluster formation has been provided by X-ray and neutron diffraction experiments [6,7]. Willis and co-workers [8–10] studied UO_{2+x} single crystals by neutron diffraction in the range of temperatures from 20 to 1100 °C, and compositions from $x = 0$ and $x = 0.25$ (U_4O_9). In Ref. [8], authors report measured displacements of the oxygen ions from the perfect tetrahedral site symmetry along <1 1 0> and <1 1 1> directions (respectively, called O′ and O″ ions). The displacements from the centre of the large interstices in the $UO_{2.13}$ fluorite structure were found to be $0.85 \cdot 10^{-10}$ and $1.05 \cdot 10^{-10}$ m. The estimated concentrations of different types of O-ions give the formula: $U_{1.0}O_{1.82}O'_{0.08}O''_{0.23}$.

Later, Willis [9] applied a more sophisticated approach to interpret his neutron diffraction data [8], and the new analysis of $UO_{2.13}$ gives an improved formula: $U_{1.0}O_{1.87}O'_{0.13}O''_{0.12}$, corresponding to approximately equal concentrations of O′ and O″. Willis suggested the simplest hypothetical geometry of a double cluster, explaining the equality of both observed displacements (2:2:2 cluster [9]). This hypothesis was discussed and tested in many other experimental studies and theoretical calculations. Blank and Ronchi [6] studied this problem using electron diffraction. Murray and Willis [7] confirmed that the solid solution accommodates clusters of O-ions of these types.

Below 1400 K, the regularly clustered excess oxygen ions tend to precipitate in an ordered phase of composition U_4O_{9-y}. This phase is characterized by an extra-oxygen superlattice superimposed to a fluorite sublattice, where some small relaxations of the uranium ions from the original FCC positions are suggested by the results of X-ray and neutron scattering measurements.

The approximate structure of the β-phase of U_4O_9, stable from 353 to 873 K, was determined by Bevan et al. [10], who showed that the U ions occupy positions close to those of the fluorite lattice of UO_2 and that the additional O-ions are accommodated in cuboctahedral (CO) clusters. Cooper and Willis [11] refined the structure model of β-U_4O_9, showing that the centres of the clusters, occupied by single O-ions in the original model of Bevan et al. [10] are actually unoccupied.

Allen and Tempest [12] suggested that cuboctahedral clusters may be present in UO_{2+x} disordered solid solution as well. Their structure includes only oxygen ions displaced along <1 1 0> from

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doi:10.1016/j.jnucmat.2009.01.029

the interstitial sites. Finally, the relative concentrations of ions displaced along <1 1 0> (O′) and along <1 1 1> directions (O″) appears to be a fundamental, distinguishing factor in the defect configuration in urania.

X-ray experiments provide important information about the influence of stoichiometry on the variation of the FCC lattice parameter as a function of temperature and stoichiometry, $a = a(T,x)$. We shall see in the following sections that these experimental data are of great importance for the assessment of interatomic potential models and for the discrimination of theoretical hypothesis concerning possible defects and defect structure and clustering.

Original studies on the variation of the FCC urania lattice parameter a with the deviation from stoichiometry, x, date back to the fifties and are due to Groenvold [13] and Perio [14], with this latter proposing a linear equation:

$$a(x) = a(0) + c\,x, \qquad (1)$$

where $a(0) = 5.469 \cdot 10^{-10}$ m is the lattice parameter of $UO_{2.00}$, and $c = (\mathrm{d}a/\mathrm{d}x)_{x=0}$ is negative, i.e., addition of extra-oxygen leads to a contraction of the UO_{2+x} lattice parameter. According to Perio [14], the contraction factor is $c = -0.12 \cdot 10^{-10}$ m. The linear trend of $a(x)$ was confirmed by Teske et al. [15], who, however, recommended a different value of the contraction factor ($c = -0.132 \cdot 10^{-10}$ m). One should note that both temperature and stoichiometry limits of validity of Eq. (1) are unknown. According to the recent phase diagram models [5], no finite domain of equilibrium solid solution UO_{2+x} exists below $T = 600$ K. Actually, samples quenched from high temperature and kept at room temperature appear to be in a metastable state, which may retain the composition and defects structure inherited from the initial state. Most likely, Eq. (1) is valid for metastable quenched samples at moderately elevated temperatures and small x.

Measurements of Rachev et al. [16], Belbeoch et al. [17] and Touzelin and Dode [18] performed at elevated temperatures (1000–1150 °C) show an approximate linearity of $a(x)$ up to $x = 0.125$, but the absolute value of the lattice contraction factor at these temperatures is markedly smaller ($c \sim -0.07 \cdot 10^{-10}$ m). At temperatures higher than 1500 K, the contraction factor is unknown. Therefore, it is unclear whether the decrease of its absolute value continues with the increase of temperature. A theoretical justification of this trend is closely related to the type and stability of the defects clusters, and is among the main objects of the current study.

The stability of interstitial dimer-clusters of the type proposed by Willis [7,8] was confirmed in static atomistic calculations, based on semi-empirical potential models, initiated by Catlow [19] and continued by Catlow and co-workers [20]. This author was the first to calculate the equilibrium structure and formation energy of different types of defects and clusters in UO_{2+x} within the framework of an ionic model [19]. The potential parameters were obtained by using results of molecular orbital calculations and bulk properties of UO_2 crystal. In static calculations, different neutralization schemes of U^{5+}ions were proposed [19,20]. This approach is a reasonable approximation at very low temperatures, at which polarons hopping is extremely rare. We shall refer this approximation for short as LPA (Localized Polaron Approximation). The Catlow's model is in good agreement with low-temperature experimental data. At a fixed lattice parameter, LPA and Mott–Littleton approximation [21] make it possible to correctly reproduce the isothermal compressibility and the phonon spectra.

A new set of interionic potentials was proposed by Jackson et al. [20] and applied to the simulation of defects and defect clusters. In hyperstoichiometric UO_{2+x}, these authors considered, along with interstitial dimers, also cuboctahedral tetramers, and calculated the entropies of the defect formation and the static migration barriers. Furthermore, other types of defects, which may appear in non-stoichiometric uranium oxide, were discussed in the literature. Especially, propagation of cluster chains in different crystallographic directions was investigated by Allen and Tempest [12].

Despite success achieved in non-empirical calculations (see Ref. [22]) and static simulations of non-stoichiometric solid, based on ionic model with semi-empirical potentials [19,20], a number of problems remain unsolved. In the next section, we develop an extension of the interionic potentials, as recently proposed [23] for hyperstoichiometric uranium dioxide. Results of static calculations are presented in Section 3.

The most important objective is to predict the high-temperature behaviour of non-stoichiometric ionic systems. In fact, the main difficulty in computer simulation of high-temperature non-stoichiometric solids is the formulation of the electron–phonon interaction responsible for electronic disorder. Molecular dynamics simulations require an explicit accounting of the individual charge state of uranium atoms. In contrast with stoichiometric UO_2, this charge state is not constant but depends on the local charge equilibrium created around oxygen vacancies or interstitials. The charge-lattice coupling causes correlations between the charge position and the local lattice deformation associated to defects. Such entities in ionic crystals are referred to as 'small polarons' [24]. At low temperatures these polarons have tendency to self-trap themselves in localized states and hence the above mentioned 'Localized Polaron Approximation' (LPA) may be useful; at higher temperatures, however, they exhibit effective mobility via hopping mechanisms, and this effect must be taken into account. Under these conditions, the fluctuations of charge states of the cationic surround may play an important role, especially in affecting dynamic properties such as electric conductivity, diffusion, and heat conduction. The general approach based on polaron theory [24], may serve here as a clue but, due to its complexity, was never implemented, to our knowledge, in conventional molecular dynamics simulations.

In Section 4, we propose a solution based on so-called polaron 'Free Hopping Approximation' (FHA). Within this approximation the excess positive charge located on an U^{5+} ion in the hyperstoichiometric dioxide jumps freely from one cation to another, equilibrating the cationic system. One of the goals of this study is an assessment of FHA applicability in molecular dynamics (MD) simulation of hyperstoichiometric uranium dioxide.

In Section 5, we investigate the effect of defects clustering in a wide temperature range, we estimate the limits of the cluster stability and we reveal how their decay affects UO_{2+x} properties, first of all the lattice parameter. These results are presented in Section 6 and are summarized in the last section.

2. Extended partly-ionic model for non-stoichiometric $UO_{2\pm x}$

In the ionic model of the non-stoichiometric $UO_{2\pm x}$, the overall neutrality is maintained by disproportionation equilibrium: any extra (neutral) oxygen atom entering this system must ionize up to O^{2-} and the two extra electrons needed must be provided by the next-neighbouring cations, which are excited to a higher ionization level. In this work, like in most other studies [19,20], we suppose that the highest ionization state is limited to U^{5+}. Correspondingly, one extra oxygen initiates the reaction:

$$1/2O_2 + 2U^{4+} \rightarrow O^{2-} + 2U^{5+}.$$

The partly-ionic potential model [23] used in this work includes Coulombic and short-range repulsive contributions for all pairs of ions existing in the $UO_{2\pm x}$ system: O^{2-}, U^{4+}, U^{5+} (or U^{3+}). Covalent forces are assumed to act between oxygen and uranium ions only.

The pair interionic potential of the ith and jth ions consists of Coulombic and short-range terms, like in the stoichiometric case [23]:

$$\Phi_{\alpha\beta}(r_{ij}) = \Phi^{(C)}_{\alpha\beta}(r_{ij}) + \Phi^{(S)}_{\alpha\beta}(r_{ij}). \tag{2}$$

The Coulombic interionic potential of the ith ion of αth type, and of the jth ion of type β is given by:

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

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

The short-range interionic interaction potential is written in the form:

$$\Phi^{(S)}_{\alpha\beta}(r_{ij}) = \Phi_O(r_{ij}) + \Phi_B(r_{ij}) + \Phi_D(r_{ij}). \tag{4}$$

The potential energy $\Phi_D(r_{ij})$ of dispersion (van der Waals attraction) forces is represented by a simple inverse-power function:

$$\Phi_D(r_{ij}) = -C_{\alpha\beta}/r_{ij}, \tag{5}$$

and $\Phi_D(r_{ij})$ is attributed to O–O interaction only. Short-range overlap (exchange) repulsion $\Phi_O(r_{ij})$ of closed electronic shells is characterized by an exponential term:

$$\Phi_O(r_{ij}) = A_{\alpha\beta} \exp\left(-\frac{r_{ij}}{b_{\alpha\beta}}\right). \tag{6}$$

The energy of covalent bonding $\Phi_B(r_{ij})$ is attributed only to U–O interactions and represented by the Morse function:

$$\Phi_B(r_{ij}) = D_{\alpha\beta}\left[\exp\left(-2\beta_{\alpha\beta}(r_{ij} - r^*_{\alpha\beta})\right) - 2\exp\left(-\beta_{\alpha\beta}(r_{ij} - r^*_{\alpha\beta})\right)\right]. \tag{7}$$

Potential parameters of this partly-ionic model for UO_2 [23] are presented in Table 1.

The partly-ionic model is applicable to any type of non-stoichiometric U–O system, but in this paper, we consider the hyperstoichiometric case only. In the extended model version, three new constants: D_5; β_5, and r^*_5 appear in addition to the prior parameters (Table 1), where index 5 corresponds to the U^{5+}–O^{2-} interaction. Further simplification follows from the physical meaning of the U–O covalent contribution Eq. (7). Supposing at long distances the covalent U^{5+}–O^{2-} interaction be the same as for U^{4+}–O^{2-}, one gets $\beta_5 = \beta_4$, and

$$D_5 = D_4 \exp\left(\beta(r^*_5 - r^*_4)\right). \tag{8}$$

Here, index 4 corresponds to the U^{4+}–O^{2-} interaction (see Table 1). This assumption makes it possible to reduce the set of new parameters to the single r^*_5. To define this additional constant, we fitted the known lattice parameter of the β-phase of U_4O_9. This phase is stable from 353 to 873 K and was carefully studied by Bevan et al. [10], Cooper and Willis [11], and others researchers, mainly by means of neutron scattering technique. It was found that the additional O-ions in the β-U_4O_9 structure are accommodated in cuboctahedral clusters. Cooper and Willis [11] have shown that the centres of these clusters are actually unoccupied. The fundamental reflections reveal [11] the contents of the average cell of edge $a(U_4O_9)$: this may be represented by joining 64 FCC subcells in a $4a_0 \times 4a_0 \times 4a_0$ supercell.[1] The total number of U ions in this supercell is 256, the total number of O-ions 576.

To simulate this structure, we created a simplified model supercell consisting of 256 U ions forming a FCC structure with 64 cuboctahedral O clusters whose centres form a cubic BCC structure. Each cuboctahedron (CO) is surrounded by six U^{5+} ions placed in the centres of all sides of the CO's. Two additional U^{5+} ions per subcell are placed inside the fluorite-structured cubes.

It was found that the measured difference of the lattice parameters $\Delta a = a_0 - a(U_4O_9)/4$ [5,13] is nearly constant ($\Delta a \sim 0.03 \cdot 10^{-10}$ m) and is well reproduced at a fixed temperature T = 773 K when $r^*_5 = 2.1 \cdot 10^{-10}$ m. Substituting this value into Eq. (8) one gets r^*_5 = 0.849 eV. These potential parameters, together with those listed in Table 1, have been used in all static and dynamic calculations described below.

Table 1
Potential parameters of the partly-ionic model for UO_2 [23] (ionicity ζ = 0.5552).

Ion pairs	A_{ij} (eV)	b_{ij} (10^{-10} m)	C_{ij}	D_{ij} (eV)	β_{ij}	r^*_{ij} (10^{-10} m)
O^{2-}–O^{2-}	883.12	0.3422	3.996	0	–	–
U–U	187.03	0.3422	0	0	–	–
U^{4+}–O^{2-}	432.18[a]	0.3422	0	0.5055[a]	1.864	2.378

[a] In Table 1 of the original paper [23] these values were incorrect. Authors are grateful to all who pointed our attention to these misprints.

3. Calculation of formation energy and geometry of defects and clusters

In this work, the formation energy E_f of all clusters is calculated within LPA as the difference between the energy of the relaxed cell, which contains all extra O^{2-} and U^{5+} ions placed as far as possible one from another and the energy of the relaxed cell containing clusters studied in their most favourable U^{5+} environment. All calculations were carried out, by using the fast method of computing Coulomb contribution [25], and a large simulation cell ($20a_0 \times 20a_0 \times 20a_0$, $N_i = 12\,000 + n_{extra}$ ions) with periodical boundaries.

3.1. 'Single-oxygen' cluster

The simplest defect in the hyperstoichiometric domain is the interstitial single extra-oxygen O^{2-} ion, neutralized by two U^{5+} ions [19]. This extra oxygen ion was placed into the interstitial site near the simulation cell centre, and all U^{5+} positions were tested to find one, which delivers the minimal energy to the relaxed cell. It was found that the most favourable configuration for the 'single oxygen' cluster does not correspond to the nearest-neighbour location of U^{5+} ions, but to the second uranium coordination shell of the extra O^{2-} ion. Its (LPA) formation energy was estimated to be[2] E_f = 1.04 eV. Note that, a substantial value of the formation energy of this 'single oxygen' cluster does not guarantee its stability. First, relative concentration of these defects may be appreciable only at extremely small x, because clusters that are more complex show much higher formation energy per single extra oxygen. Secondly, at high temperatures (where only the hyperstoichiometric solid considered is thermodynamically stable), the LPA approach fails, and polarons hopping essentially decreases the stability of all clusters, including 'single oxygen'.

3.2. Interstitial dimers

Two extra oxygen ions placed into the simulation cell, may form a 'double oxygen cluster' or an interstitial dimer (we call here this type of cluster 'Willis cluster' [8]). In LPA, there exist a wide variety of neutralization schemes for this cluster, including those with four neutralizing U^{5+} ions localized in the vicinity of interstitial oxygen,

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[1] Here and below $a_0 = a_0(T)$ denotes the lattice parameter of stoichiometric UO_2 at given temperature.

[2] The nearest-neighbour location of U^{5+} ions gives also a stable configuration with formation energy of only ~0.3 eV. The energy loss is apparently is due to increase of additional mutual repulsion of U^{5+} ions, which come closer in this configuration.

Table 2
Static formation E_f and binding E_b energies (in eV) of the interstitial double clusters for different neutralization schemes ($n(U^{5+}) = 4$) calculated within LPA at large cell size ($N = 12002$ ions) with a lattice parameter $a = 5.47 \cdot 10^{-10}$ m.

Neutralization scheme	n_{int}	n_{vac}	Cluster type	E_f	E_b
Small tetrahedron (*sT*)	6	4	2:4:4	3.72	1.64
Small rhombohedron (*sR*)	4	2	2:2:2	2.56	0.48
Elongated rhombohedron (*eR*)	3	1	2:1:1	2.55	0.47

and those, which include some distant U^{5+} ions. The first type of Willis clusters may be considered as a neutral, the other as a charged (incompletely neutralized) one.[3]

The LPA-neutralizing schemes for (neutral) Willis clusters may differ essentially in the spatial location of neighbouring U^{5+} ions. It was found that, within the extended partly-ionic model, there exist a number of schemes having comparable formation energy E_f. The static formation E_f energies, the numbers of interstitial oxygen n_{int} and of vacancies n_{vac} calculated at a fixed lattice parameter of $5.47 \cdot 10^{-10}$ m for three types of neutralization schemes giving the most stable neutral double clusters, are presented in Table 2 and shown in Fig. 1.

The neutralization scheme, marked as *sR* (small rhombohedron) corresponds to the 2:2:2 Willis cluster (two extra oxygen + two displaced lattice oxygen + two lattice vacancies), and delivers formation energy (~2.6 eV) high enough to explain effective formation of stable dimers of this type. This cluster contains both <1 1 0> (O′) and <1 1 1> (O″) interstitials, but is not the most stable one predicted by the extended partly-ionic model. Actually, the maximum formation energy corresponds to the *sT* (small tetrahedron) neutralization scheme, producing cluster of six interstitials and four vacancies (2:4:4 dimer: two extra oxygen + four displaced lattice oxygen + four lattice vacancies) shown in Fig. 1.

Its formation energy is more than 1 eV higher and the binding energy (see Table 2) $E_b = E_f(\text{dimer}) - 2E_f(\text{single})$ is several times larger than that of Willis 2:2:2 cluster. At the same time, 2:4:4 cluster has only one type (O′) of interstitial displacement from the interstitial sites centres $(1.16 \pm 0.10) \cdot 10^{-10}$ m along a <1 1 0> direction.

Another *eR* (elongated rhombohedron) neutralization scheme produces 2:1:1 clusters (two extra oxygen + one displaced lattice oxygen + one lattice vacancy), having almost the same formation energy as the 2:2:2 (*sR*) cluster, however its three O″ interstitials are <1 1 1>-displaced from the interstitial sites centres at $(0.83 \pm 0.10) \cdot 10^{-10}$ m.

3.3. Interstitial tetra- and pentamer cuboctahedral clusters

The formation of stable (or metastable) globular defect clusters having cuboctahedral structure was discussed by several authors [10–12,20]. Such clusters were found emerging spontaneously during fast cooling of thermally shocked stoichiometric UO_2 solid in our earlier simulations. In the non-stoichiometric U–O system, globular structures become more stable due to presence of excess interstitial ions. At higher concentrations of extra oxygen ions, these clusters form regular spatial superstructures, which eventually merge in the supercell structures characteristic for U_4O_9 ordered phases [11].

The simplest cuboctahedral (CO) clusters are produced by four extra oxygen ions penetrating into the large interstices and displacing eight adjacent lattice oxygen to the neighbouring interstitial positions. Actually such cluster consists of twelve interstitials and eight vacancies bound together (or four extra oxygen and eight oxygen Frenkel pairs). In this (tetramer) defect structure, which we denote below as CO(12), the central interstitial position is empty and is able to accommodate an extra oxygen forming pentamer globular cluster CO(13).

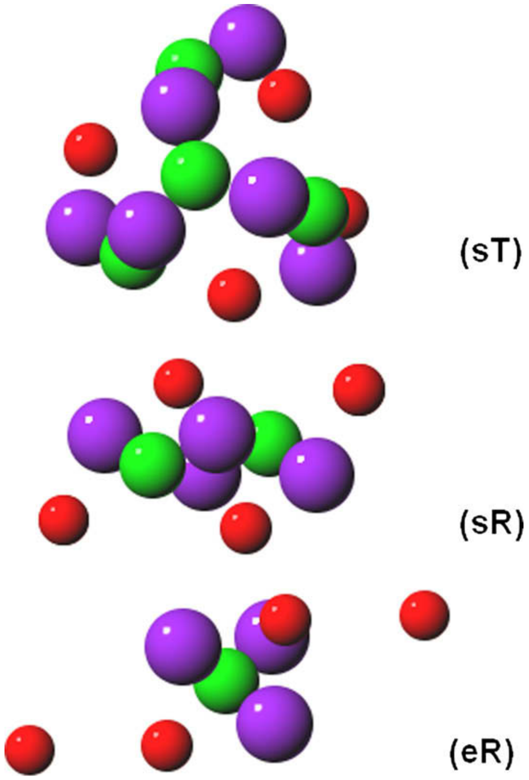

Fig. 1. Equilibrium structure of the dimer-clusters for different neutralization schemes: (*sT*) – 2:4:4 cluster; (*sR*) – 2:2:2 cluster; (*eR*) – 2:1:1 cluster. Small red spheres represent positions of U^{5+} ions, larger green spheres show vacant oxygen lattice sites, and largest violet spheres indicate relaxed positions of the interstitial oxygen ions.

Modelling globular clusters within LPA requires, like in the case of Willis dimers, testing different competing neutralization schemes. The static calculations performed for CO(12) and CO(13) clusters reveal that the maximum formation energy in both cases corresponds to the charged symmetric clusters, neutralized by six nearest U^{5+} ions placed in the centres of the surrounding cube faces. The formation energy of such clusters was estimated as 13.2 eV for CO(12) ($4O^{2-} + 6U^{5+}$, charge 2 in O^{2-} charge units), and 12.2 eV for CO(13) ($5O^{2-} + 6U^{5+}$, charge 4 in O^{2-} charge units). Hence, according to the applied model, cuboctahedral clusters are much more stable than dimers. Their formation energy (in eV per single extra oxygen) is: 3.3 for CO(12) and 2.4 for CO(13) compared to 1.3–1.9 for different types of dimers.[4] Both CO(12) and CO(13) clusters have only one type of interstitials (O′) displaced from their sites centres of $\sim 1.1\text{–}1.2 \cdot 10^{-10}$ m. The comparison of calculated static formation energies of completely neutralized clusters is presented in Table 3 together with calculations by Catlow [19] and Jackson et al. [20].

4. Free hopping approximation for MD simulation

Static calculations give important information on the defects relative stability at $T = 0$ but they are irrelevant [19] to experimen-

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[3] The same is true for any other cluster within LPA. Below the cluster charge is expressed in units of O^{2-} ion charge. For example, Willis cluster neutralized by only two neighbouring U^{5+} ions, is regarded as having charge 2.

[4] A test of the results sensitivity to the partly ionic model parameters shows that the relative stability and structure details for different defects might change but general conclusions remain the same.

Table 3

Formation energy of clusters (in eV per excess O^{2-}) calculated within LPA by using a large simulation cell ($20a_0 \times 20a_0 \times 20a_0$) with periodical boundaries, and comparison with the results of calculations of Catlow [20] and Jackson et al. [21].

No.	Defect (cluster) type	Catlow [19]	Jackson et al. [20]	This work
1	Single extra oxygen ($O^{2-} + 2U^{5+}$)	1.11	−0.45[a]	1.04
2	Neutral dimer (Willis 2:2:2)[b]	1.75	1.13	1.28
4	Neutral cuboctahedron ($4O^{2-} + 8U^{5+}$)	–	1.64[c]	3.07

[a] Neutralized by two nearest U^{5+} ions – unstable.

[b] (sR) Neutralization scheme.

[c] Maximum value.

tal high-temperature conditions. At temperatures higher than 1000–1500 K, oxygen diffusion and polaron-hopping processes are largely activated and LPA fails to describe the behaviour of the cationic sub-system [26].

In this work, we propose a high-temperature approximation, called 'Free Hopping Approximation' (FHA), where the hole (excess positive charge located on U^{5+} ion) in the hyperstoichiometric dioxide (or excess electron of U^{3+} in the hypostoichiometric case) may jump from one lattice cation position to another.

Within FHA, in contrast to LPA, the lattice positions of U^{5+} are not fixed, FHA allows for periodic jumping of electronic holes located on U^{5+} ions. Electronic holes jump periodically into positions of neighbouring U^{4+} lattice ions, where instantaneous values of electric potential are minimal. The frequency of such hopping is arbitrarily fixed,[5] but must be high enough to imitate the cationic disorder and simulate fast continuous fluctuations in the electronic sub-system [19]. Some physical conditions must be, therefore, respected: this frequency must be much higher than the effective frequency appearing in the oxygen diffusion coefficient, and much lower than the frequency of the ionic displacements in MD simulation.

The algorithm of free hopping, implemented in our MD simulation program, allows for hopping of one hole, located on a U^{5+} ion – that has the highest electric potential among all such ions in the cell – every fixed period Δt_h, taken shorter than the characteristic diffusion time τ_D ($\tau_D = a^2/D^0$). Under simulation conditions, the oxygen diffusion coefficient, D^0, in UO_{2+x} vary from 10^{-8} to $10^{-5}\,cm^2\,s^{-1}$, and the jumping distance a can be taken equal to the FCC lattice parameter ($\sim 5.5 \cdot 10^{-10}$ m); this corresponds to values of τ_D comprised in the interval $3 \cdot 10^2$–$3 \cdot 10^5$ ps. On the one side, the simulation process slows down if the frequency f_h is too high; on the other, a lower frequency may cause problems with the relaxation of Maxwell velocity distribution in the time interval between two consecutive hopping events. Additional tests reveal that the calculation results are insensitive to the hopping frequency in a broad range of intermediate values. We performed the reported calculations with $\Delta t_h \sim 10$–20 *fs*.

5. MD simulation of hyperstoichiometric UO_{2+x} solid

A number of MD computer simulations were carried out by using the extended partly-ionic model and FHA to study the behaviour of hyperstoichiometric UO_{2+x} solid at temperatures $1000\,K < T < 2700\,K$ and $0 < x < 0.25$. The procedure was as follows:

- randomly distributed multiple defects were created and relaxed near the cell centre;
- then the conventional Nosè-Hoover NPT-ensemble MD simulation procedure, was started based on a fast method of computing Coulomb contributions [25];
- the defects structure, equilibrium lattice parameter, oxygen diffusion coefficient, as well as thermodynamic properties such as thermal expansion, compressibility and heat capacity were computed as described in Ref. [23].

In this context, the MD simulations reveal the importance of polaron-hopping effects in the evolution of defect structures and in the mechanisms of ionic diffusion at high temperatures. The first polaron-hopping effect is to change the overall cluster structure with a shift of equilibrium between different types of clusters.[6] Within the FHA, the initial neutralization scheme is destroyed after a few picoseconds. The cluster charge fluctuates continuously, and can be estimated only on the average. For example, the mean charge of the Willis cluster is around one (in O^{2-} charge units), and the average charge of cuboctahedral tetramer is between three and four. Polarons hopping does substantially decrease the bonding energy of the CO(12) clusters. On the contrary, CO(13) clusters, less stable according to LHA, become more stable under dynamic conditions and emerge spontaneously within a few picoseconds, remaining the most stable type of cluster up to 1500–1700 K.

When the simulation starts from a set of randomly distributed CO(12) clusters, a typical observed event is the fluctuation of the local charge distribution around cuboctahedral tetramers, initiating formation of oxygen Frenkel pairs, whose vacancy migrates independently, giving rise to an extra (oxygen vacancy) diffusion mechanism; the remaining interstitial ions do finally join the initial cluster, forming a CO(13) pentamer.

An additional point, which may be important for the explanation of the observed cuboctahedral structures configuration in β-U_4O_9, is the rather flexible location of the central interstitial in the CO(13) pentamers. This may be explained by the flatness of the potential due to the presence of a rather weak electric field produced by fluctuations of the polaron concentration. Due to existing hopping barrier (about 0.3 eV [26]), these fluctuations at low temperatures may exist for quite a long time, enough to produce the displacements observed in spectroscopic experiments [8,9].

An important test of the adequacy of the extended ionic model is provided by the neutron diffraction experiment performed by Willis [8,9] at $T = 800\,°C$ and $O/U = 2.13$. We carried out special MD runs for these experimental conditions to test the ability of the model to reproduce the overall concentration of interstitial ions and the relative concentrations of O' and O'' oxygen.[7] The model predicts a much more complex picture than expected. Fig. 2 presents a typical snapshot of the defect structure during one of these MD simulations. There prevail cuboctahedral pentamers CO(13) and 2:1:1 dimers, containing, chiefly, O'-type oxygen. The experimental values of the overall relative concentrations of the occupied interstitial sites are approximately 1.82 [8,9], i.e. each extra oxygen produces one or more lattice vacancies and, correspondingly, lattice oxygen displaced into interstitial positions. Our simulation gives 1.87 ± 0.01 in a good agreement with the experiment.

The agreement between the predicted relative concentrations of O' and O'' oxygen is less satisfactory. Results of our MD simulations give the formula: $U_{1.0}O_{1.87}O'_{0.17}O''_{0.08}$, with average displacements of $1.08 \cdot 10^{-10}$ m (O') and $1.04 \cdot 10^{-10}$ m (O''). This indicates an

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[5] Hence, FHA is inapplicable in calculation of electric conductivity, which is proportional to the frequency of polarons hopping.

[6] The evolution of the defect structure and concentration within FHA was studied using visualization JMol software (http://jmol.sourceforge.net).

[7] At high temperature, interstitials may be displaced in any direction from the centre of the large interstices and their classification into of O' and O'' types is rather conditional. In our simulation, the interstitial was marked as belonging to O' type, if the projection of its displacement vector on <1 1 0> direction is larger than on <1 1 1> direction, and *vice versa*.

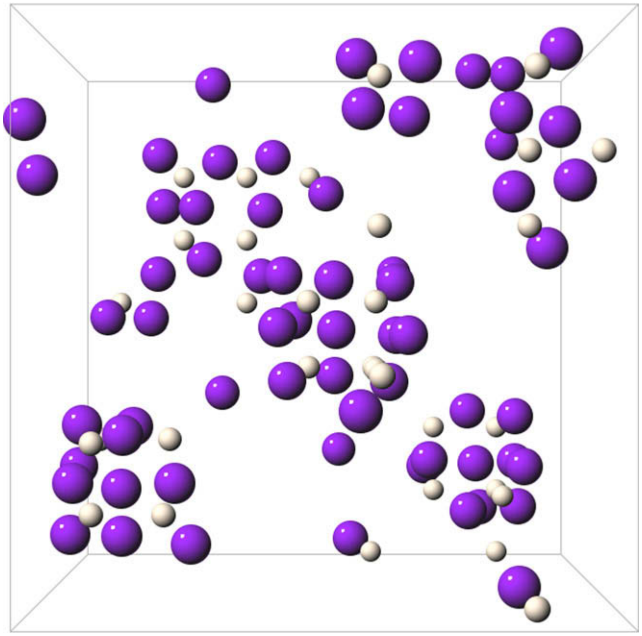

Fig. 2. Typical snapshot of the UO_{2+x} lattice defect structure at $T = 800$ °C and $O/U = 2.13$. Big spheres show instantaneous positions of oxygen near interstitial sites; small white spheres indicate vacant lattice positions. The tendency to formation of cuboctahedral pentamers is clearly seen.

overestimation of the concentration of the O′-oxygen and an underestimation the concentration of the O″-oxygen. In Fig. 3 our results are compared with the first estimation of Willis [8]: $U_{1.0}O_{1.82}O'_{0.08}O''_{0.23}$, and to his refined result: $U_{1.0}O_{1.87}O'_{0.13}O''_{0.12}$ [9]. This requires an additional detailed analysis of both experimental and simulation data.

A typical snapshot of the defect structure presented in Fig. 2 illustrates the reason of this discrepancy. The ionic model predicts much more complex defects clusters picture in the hyperstoichiometric dioxide, where cuboctahedral pentamers and 2:1:1 dimers, having chiefly O′-type oxygen, prevail.

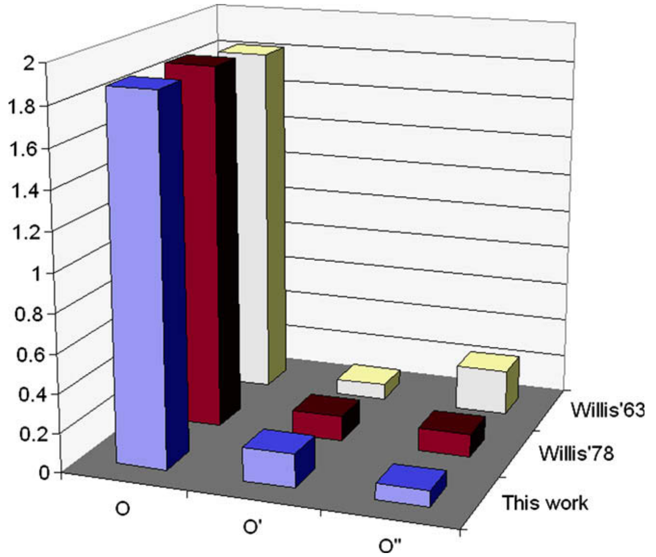

Fig. 3. Comparison of the predicted interstitial structure of UO_{2+x} at $T = 800$ °C and $O/U = 2.13$ with the first estimation of (Willis'63) [8] and his refined result (Willis'78) [9].

6. Effect of stoichiometry on lattice parameter of UO_{2+x}

The effect of lattice contraction in hyperstoichiometric uranium dioxide is very well known as a useful indicator of deviation from stoichiometry [27]. From the other side, this effect is one of the most difficult to explain on the basis of theoretical calculations [19,20,29]. Lattice contraction is a small effect, which is extremely sensitive to the clusters structure and to details of the potential model used in simulation. Only a few attempts to estimate this value by MD simulation are known [29]. One of the main objectives of the current study is to estimate this effect by using an ionic model and MD simulation technique to predict properties of solid $UO_{2\pm x}$ at high temperatures where experimental data are missing.

Nosè-Hoover simulation technique gives the equilibrium value of the average uranium FCC lattice parameter, which at least at small x, can be compared directly with existing experimental X-ray data and empirical correlations [13–18]. Nevertheless, this approach is in practice difficult to apply, because the small effect of non-stoichiometry on the lattice parameter is comparable to the uncertainty of predictions from simulations carried out with different MD cell sizes. Hence, instead of the absolute value of the lattice parameter, we examined the difference between the lattice parameter of UO_{2+x} and that of UO_2: $\Delta a = a(x) - a_0$.

Existing empirical correlations of Perio [14] and Teske et al. [15] assume a simple linear dependence of $a(x)$ as in Eq. (1). This is unquestionably correct only at small x. Therefore, the most straightforward way to estimate Δa is to simulate in parallel non-stoichiometric dioxide and stoichiometric UO_2 at the same temperature and with the same MD cell size.

We performed a number of such parallel simulations with different stoichiometry and cell sizes ranging from hundreds to several thousands of ions, where the majority was carried out on MD cell of different size (from $6a_0 \times 6a_0 \times 6a_0$, $N_i = 768 + n_{extra}$ ions to $12a_0 \times 12a_0 \times 12a_0$, $N_i = 2592 + n_{extra}$ ions). In Fig. 4 the existing

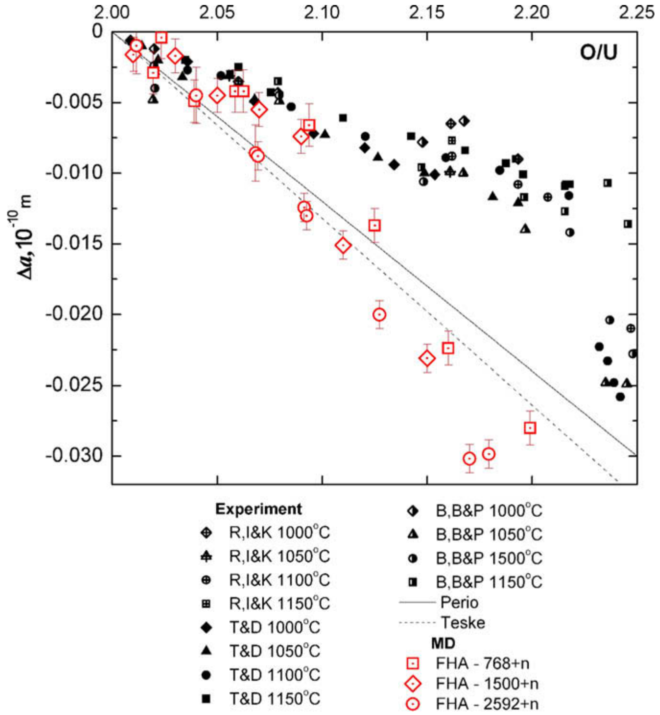

Fig. 4. Comparison of the FHA–MD simulation of UO_{2+x} lattice contraction at $T = 1050$ °C with experimental data of Rachev et al. [16], Belbeoch et al. [17], Touzelin and Dode [18] at $T = 1000–1150$ °C.

experimental data, in the interval $T = 1000–1150\ °C$, of Rachev et al. [16], Belbeoch et al. [17] and Touzelin and Dode [18] are plotted together with the FHA–MD simulation results at $T = 1050\ °C$. As one can see, at small stoichiometry deviations ($x < 0.1$) there exists an overall good agreement between experimental data and simulation results. At higher stoichiometry deviations, the extended ionic model predicts remarkably larger lattice contraction and is in better agreement with the correlations of Perio and Teske et al. [14,15].

The high-temperature predictions of the lattice contraction effect for $x < 0.1$ is presented in Fig. 5. With increasing temperature the lattice contraction decreases and at $T > 1400$ K, the lattice parameter surprisingly becomes even higher than in stoichiometric UO_2. This effect of lattice expansion is characteristic for interval $1500 < T < 2000$ K and is the more pronounced, the smaller is x. The analysis of MD data shows that this effect is related to the decay of the pentamer CO(13) clusters, stable at lower temperatures, and to the growing compressibility of the high-temperature solid. At higher temperatures, the concentration of CO(13) clusters drops, and at $T > 2000$ K becomes negligible. Here the contraction factor is remarkably greater than in the temperature range $T < 1500$ K. The decay of CO(13) clusters is reflected by a raise of the relative concentration of interstitial oxygen (Fig. 6), in a peak of the heat capacity (Fig. 7) and in an abrupt change of the apparent activation energy of the oxygen diffusion coefficient from 0.4 eV ($T < 1400$ K) to 0.8 eV ($T > 1600$ K).

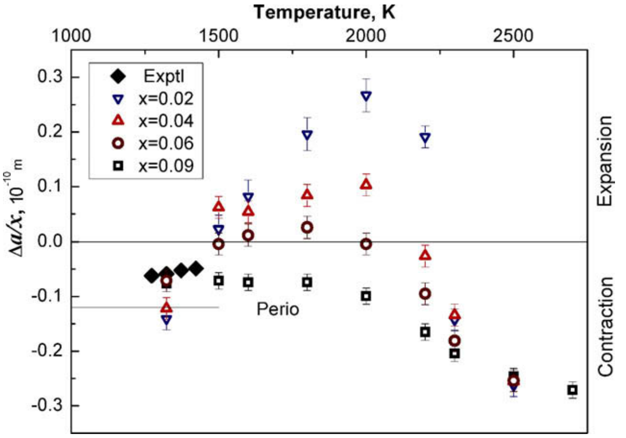

Fig. 5. Predicted UO_{2+x} lattice contraction factor versus temperature at several stoichiometry (small x). Solid diamonds symbolize values obtained from experimental data of Touzelin et al. [18] ($x < 0.06$), open symbols represent MD simulation results.

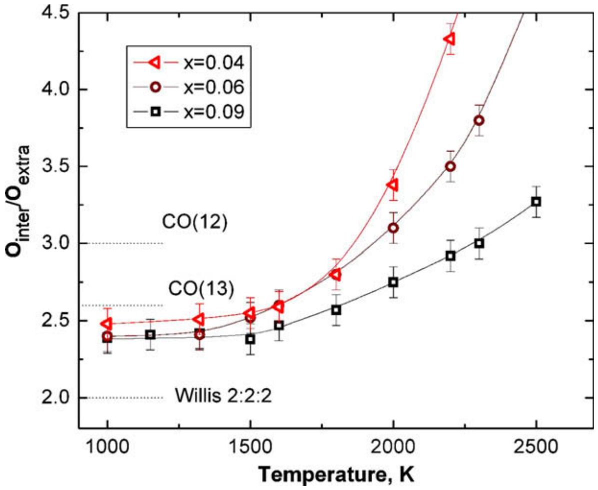

Fig. 6. Ratio of oxygen interstitial to extra oxygen ions in hyperstoichiometric solid versus temperature at various x. Low-temperature limits corresponding to the Willis 2:2:2 dimers, cuboctahedral tetramers CO(12) and pentamers CO(13) are shown as horizontal dotted lines.

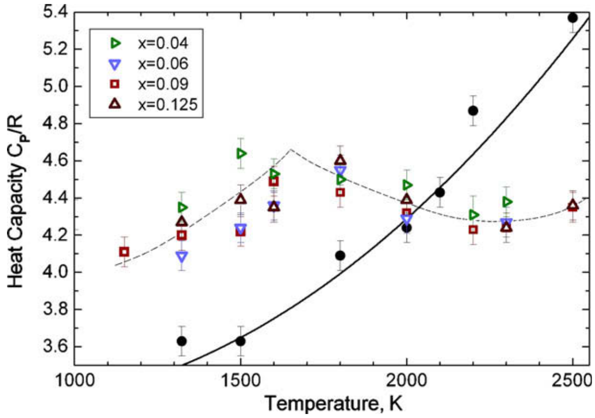

Fig. 7. Computed isobaric heat capacity per ion (MD simulation, ideal-gas contribution [28] included). Hyperstoichiometric UO_{2+x} (open symbols) and stoichiometric $UO_{2.00}$ (solid circles, 768 ions per cell). Solid line represents recommended values of $UO_{2.00}$ heat capacity [28]. Dotted line is a guide for an eye.

7. Conclusions

Recently proposed interatomic potentials [23] were extended to hyperstoichiometric uranium dioxide, UO_{2+x}, and used in static and dynamic simulations. Static calculations, performed under a conventional 'Localized Polaron Approximation' (LPA), reveal that at $T = 0$ the 2:4:4 dimers are more stable than the Willis 2:2:2 clusters, whereby cuboctahedral tetra-and pentamers are more stable than any dimers.

An atomistic study of non-stoichiometric uranium dioxide under high-temperature conditions requires explicit accounting of the local charge distribution created around oxygen vacancies or interstitials. A new model of polarons hopping, called 'Free Hopping Approximation' (FHA), is proposed and implemented in the MD simulation code.

Extensive molecular dynamics simulations of UO_{2+x} solid, performed in a wide range of temperatures under FHA, reveal some new, unexpected features at high temperatures. The equilibrium lattice parameter and the concentrations of O′ and O″ interstitials were computed for different deviations from stoichiometry and compared with existing experimental data. It was shown that the polaron-hopping effect is very important for the correct prediction of the lattice parameter and other thermodynamic properties. Polarons hopping also essentially promotes all migration processes in the non-stoichiometric U–O oxide system.

At elevated temperatures ($1500\ K < T < 2000\ K$) the decay of pentamer CO(13) clusters, most stable at lower temperatures, diminishes the lattice contraction (especially at small x) and does even turn it to expansion. At higher temperatures ($T > 2000$ K) again a marked increase in the lattice contraction is predicted.

In conclusion, the extended partly-ionic model, when combined with proposed polaron FHA is able to satisfactorily describe the whole set of high-temperature properties of hyperstoichiometric UO_{2+x} solid, including the lattice contraction, the overall concentration of interstitial oxygen and lattice vacancies and the oxygen diffusion coefficients. The predicted relative concentrations of O′ and O″ ions is higher than that obtained from the analysis of neutron diffraction experiments [8,9]. MD simulations reveal, in particular, the importance of the formation and decay of cuboctahedral CO(13) clusters, whose behaviour controls the UO_{2+x} properties in a wide range of temperatures. Decay of CO(13) clusters is reflected in a typical peak of the heat capacity versus temperature, and in an increase of the oxygen diffusion coefficient and concentration of interstitial oxygen ions. This behaviour is similar to that observed near the λ-transition point in stoichiometric UO_2 [23], and implies a close analogical correspondence. These specific high-temperature features of the MD simulations, related to formation of complex instantaneous defect aggregates and giving rise to enhanced diffusion mechanisms, will be discussed in more detail elsewhere.

Acknowledgment

This work is supported by the European Commission as part of the 6th Framework Programme for Research and Technological Development, under the Service Contract No. 202039-2005-05 F1SC KAR UA.

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