

# Point defects in uranium dioxide: Ab initio pseudopotential approach in the generalized gradient approximation

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## Abstract

The stability of point defects in uranium dioxide is studied using an ab initio plane wave pseudopotential method in the generalized gradient approximation of the density functional theory. Uranium pseudopotentials are first tested in both the generalized gradient approximation and the local density approximation on metallic phases of uranium and on uranium dioxide. It is found that the generalized gradient approximation gives the best description of these materials. The energies of formation of point defects (single vacancies and interstitials, Frenkel pairs and Schottky defects) in  $\text{UO}_2$  are calculated. The values obtained lead to a reliable set of numerical data that are analyzed in the framework of the point defect model commonly used to assess defect concentrations in uranium dioxide as a function of the stoichiometry. The ability of the point defect model to accurately reproduce defect concentrations in uranium dioxide is discussed.

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## 1. Introduction

Point defects are created in actinide compounds by self-irradiation. In particular, alpha decays result in the emission of an helium nucleus and of a recoil nucleus. The recoil nucleus can acquire a kinetic energy

of the order of tenths of keV ( $\approx 70$  keV for the  $^{234}\text{Th}$  nucleus resulting from the decay of  $^{238}\text{U}$ , for instance) and by collisions with atoms in the crystal it can generate displacement cascades along its trajectory. Temperature effects favor the recombination of the defects and the recrystallization, but a large amount of point defects remains. These defects have an important influence on the physical properties of the material: they can modify the crystal structure, cause a swelling of the solid, and also constitute traps for fission gases or helium, hence influencing the diffusion properties of these latter. It is particularly important to understand the stability of

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point defects in uranium dioxide since this material is used as the standard nuclear fuel in water-pressurized reactors.

Electronic structure calculations by ab initio techniques enable to determine quantities inaccessible to experiments because of either the too small length scale or the impossibility to isolate the contribution of a given factor on the studied physical properties. In particular, ab initio calculations allow to study separately different types of point defects in a solid and to determine for each of them its stability (formation energy) or its influence on the crystal structure (atom relaxation around the defect, swelling of the crystal). These data can then be used as input in thermodynamical models at a macroscopic scale. Such an application will be done here to determine the evolution of the defect concentrations with the stoichiometry of uranium dioxide. This paper focuses on the following point defects: vacancies, interstitials, Frenkel pairs and Schottky defects.

Ab initio studies of point defects in uranium dioxide have already been published. Calculations by Petit et al. [1] and by Crocombette et al. [2] are based on the density functional theory (DFT), like the present study, but take exchange–correlation interactions into account in the local density approximation (LDA). We show here that the generalized gradient approximation (GGA) improves substantially the description of the cohesive properties of uranium and uranium dioxide. We discuss the values obtained for the formation energies in the GGA by comparison to those obtained in the LDA [2] and by experimental means. Petit et al. [1], in the first ab initio study of point defects in  $\text{UO}_2$ , moreover used the LMTO-ASA (linear muffin tin orbitals-atomic sphere approximation) method. This method does not enable to calculate the relaxed position of the atoms around the defects and leads to an overestimation of the formation energies of the defects. Crocombette et al. [2] have used a method based on plane-waves and pseudopotentials similar to the one we use here but in the LDA. Uranium vacancies were then found to be the most numerous defects in hyper-stoichiometric  $\text{UO}_2$ , which is in contradiction to experimental data [3]. The limitations of both those previous studies of  $\text{UO}_2$  hence justify the present paper.

In the following section, the calculation method is briefly presented. In Section 3, we give the results obtained for bulk metallic uranium and bulk uranium dioxide in order to test the accuracy of the pseudopotentials used. In Section 4, the results for the study of point defects are reported: the structural modifications induced by the defects and the formation energies of the defects. In Section 5 these latter results are introduced in the thermodynamical so-called point defect model (PDM) to determine the variation of the defect concentrations with deviation from stoichiometry in  $\text{UO}_2$ . The validity of this model for  $\text{UO}_2$  is discussed.

## 2. Method of calculation

To calculate the electronic structure of the investigated materials, we use a plane-wave pseudopotential method [4] based on the density functional theory (DFT) [5,6] implemented in the code ABINIT [7,8]. Pseudopotentials model the potential yielded by the nuclei and the core electrons whereas the valence electron wave functions are expanded in a plane-wave basis. The generalized gradient approximation (GGA) as parametrized by Perdew–Burke–Ernzerhof (PBE) [9] is used to describe the exchange–correlation interactions. Norm-conserving uranium and oxygen pseudopotentials [10] are generated according to the Troullier–Martins scheme [11], with the s component chosen as the local component for uranium and the p one for oxygen. The uranium pseudopotential is constructed in the atomic  $\text{U}^{2+}$  state  $6s^2 6p^6 6d^1 5f^3 7s^0$  with cut-off radii of 1.26, 1.52, 2.20 and 1.26 a.u. for the 6s, 6p, 6d and 5f valence orbitals respectively [12]. The oxygen pseudopotential is constructed with a cut-off radius of 1.45 a.u. for both 2s and 2p valence orbitals. The pseudopotentials are generated with the FHI98PP code [13].

Point defects are modelled using the supercell technique with a 120 Ry energy cut-off in the expansion of the plane wave basis. In the preliminary study of the cohesive properties of bulk metallic uranium and bulk  $\text{UO}_2$ , a 180 Ry energy cut-off was used. To improve convergence, a Gaussian smearing of the occupation number of 0.02 Ry is applied for integration in the Brillouin zone. The Brillouin zone is sampled by a  $8 \times 8 \times 8$  Monkhorst–Pack grid [14] corresponding to a mesh made of 28 k points for face-centered cubic (fcc) uranium and  $\text{UO}_2$  in the fluorite structure, 40 k points for body-centered cubic (bcc) uranium, 64 k points for orthorhombic  $\alpha$  uranium, 64 k points for body-centered tetragonal (bct) uranium. For the  $\text{UO}_2$  supercells a  $4 \times 4 \times 4$  grid is used, made of 6 k points for the 24-atom  $\text{UO}_2$  supercell, and of 10 k points for the 12-atom  $\text{UO}_2$  supercell.

## 3. Bulk uranium and bulk uranium dioxide

### 3.1. Metallic uranium

The uranium pseudopotential is tested by modeling different phases of uranium: the low pressure ground-state orthorhombic  $\alpha$ -phase, as well as the body-centered and face-centered cubic phases and the body centered tetragonal phase. Even if all these structures do not exist in the phase diagram of uranium, we will determine their relative stability and check that our approach indeed yields the  $\alpha$ -phase as the lowest energy phase. Table 1 gives the equilibrium volume  $V_0$  of the unit cell, the bulk modulus  $B_0$  and the cohesive energy  $E_{c0}$  obtained

Table 1

Equilibrium volume ( $V_0$  in a.u.<sup>3</sup>), bulk modulus ( $B_0$  in GPa) and cohesive energy ( $E_{co}$  in eV) for the orthorhombic  $\alpha$ -phase, the body-centered tetragonal phase (bct), the body-centered cubic phase (bcc) and the face-centered-cubic phase (fcc) of uranium. Results for both the GGA and the LDA [2,12] are given, as well as the experimental values if available [16,17]

	$V_0$ (a.u. <sup>3</sup> )			$B_0$ (GPa)			$E_{co}$ (eV)	
	LDA	GGA	Experimental	LDA	GGA	Experimental	GGA	Experimental
$\alpha$ -U	128	136	139	188	143	136	5.1	5.4
bct-U	–	139	–	–	127	–	5.0	–
bcc-U	129	138	–	170	121	113	4.9	–
fcc-U	134	145	–	154	116	–	4.8	–

in the GGA and in the LDA [2,12] for these structures, and the corresponding experimental values if they exist. The bulk modulus is determined by a Birch–Murnaghan fit [15] of the total energy curve as a function of the volume of the unit cell.

For the  $\alpha$  ground-state structure of uranium, the GGA substantially improves the results compared to the LDA: the error of the calculated volume relative to the experimental value decreases from 8% in the LDA to 2% in the GGA, and the error of the calculated bulk modulus drops from 38% in the LDA to only 5% in the GGA. The GGA cohesive energy is also in good agreement with the experimental value (the error amounts to 6%). The GGA pseudopotential thus gives satisfactory results for the cohesive properties of uranium, in the range of error commonly admitted for ab initio calculations.

The relative stability of the different crystal structures considered is represented in Fig. 1: for each phase the total energy is plotted as a function of the volume per atom. We indeed obtain that the  $\alpha$ -phase is the ground-state structure for uranium. The metastable phases are successively the bct phase (+0.1 eV), the bcc phase (+0.2 eV) and finally the fcc phase (+0.3 eV). It should be emphasized again that the fcc and the bct phases do not exist in the phase diagram of uranium, but a more complex tetragonal phase with 30 atoms by unit cell however appears above 942 K at ambient pressure (which was not considered here due to computer limitations), and the bcc phase appears above 1049 K [16,18].

Finally, Table 2 gives the details of the structural parameters obtained for different phases of uranium in the GGA. We recall that the  $\alpha$  structure is an orthorhombic phase with space group  $Cmcm$  and with two atoms per unit cell whose positions are given by a parameter  $y$ :

$$\vec{B}_1 = y\hat{y} + 1/4c\hat{z}, \quad (1)$$

$$\vec{B}_2 = -y\hat{y} - 1/4c\hat{z}, \quad (2)$$

where  $\hat{y}$  and  $\hat{z}$  are unit vectors of the cartesian plan. The orthorhombic  $\alpha$  structure obtained by our calculation is in very good agreement with experimental data. Our results for the  $\alpha$  structure are also in good agreement with

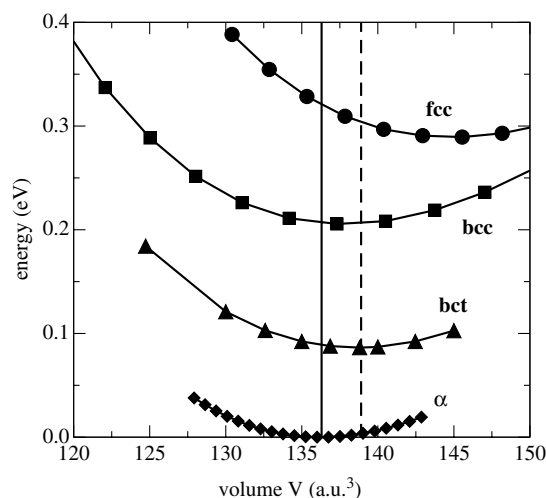


Fig. 1. Relative stability of different phases of uranium: total energy (in eV) as a function of the volume per atom (in a.u.<sup>3</sup>) for the  $\alpha$ -phase, the body-centered tetragonal (bct) phase, the body-centered cubic (bcc) phase and the face-centered cubic (fcc) phase. The energy reference is the one of the  $\alpha$ -phase in its calculated equilibrium volume represented with a vertical line. The experimental equilibrium volume of  $\alpha$  uranium is represented by the vertical dashed line.

Table 2

Structural parameters (in a.u.) obtained in the GGA for the orthorhombic  $\alpha$ -phase, the body-centered tetragonal (bct) phase, the body-centered cubic (bcc) phase and the face-centered cubic (fcc) phase of uranium, and compared to experimental data [16,19]

	GGA	Experimental
$\alpha$ -U	$a = 5.37$ $b/a = 2.02$ $c/a = 1.74$ $y = 0.10$	5.39 2.06 1.74 0.10
bct U	$a = 7.00$ $c/a = 0.81$	– –
bcc-U	$a = 6.51$	6.33
fcc-U	$a = 8.33$	–

the all-electrons ab initio calculations by Söderlind [20]. The slight differences with their results can be attributed to the spin–orbit coupling which is not taken into account in our study and which is therefore found to have a negligible influence on the calculated structural properties of uranium.

We conclude that the cohesive and structural properties of uranium are well described by our pseudopotential approach in the GGA. Neither spin–orbit coupling [20] nor an improved approximation for exchange–correlation need to be taken into account.

### 3.2. Uranium dioxide

In a similar way, the cohesive properties of uranium dioxide are calculated and compared to previous results in the LDA [2] and to experimental data. Table 3 first gives the equilibrium volume and the bulk modulus of  $\text{UO}_2$  in the GGA taking into account the p component of the oxygen pseudopotential as the local component (the local component of the uranium pseudopotential being the s component). The choice of the local component for the oxygen pseudopotential has however no big influence on the calculated lattice parameter and bulk modulus, but the p local component gives results slightly closer to the experimental data. In the following, all calculations will thus be performed with the s component as the local component of the uranium pseudopotential and the p component for oxygen.

Table 3 shows that GGA gives results in much better agreement with experimental data than LDA: the relative error of the volume decreases from 12% in the LDA to 4% in the GGA, and the one of the bulk modulus drops from 22% in the LDA to 6% in the GGA. The value obtained in the GGA for the cohesive energy is also in good agreement with the experimental data. All electron calculations by Söderlind [20] in the GGA but with the spin–orbit coupling taken into account yield a slightly larger volume of 274.9 a.u.<sup>3</sup> and a somewhat softer bulk modulus of 170 GPa for  $\text{UO}_2$ .

The substantial improvement in the description of the cohesive properties of U and  $\text{UO}_2$  compared to LDA have suggested us to reconsider the calculation of the formation energies of point defects in  $\text{UO}_2$  using the GGA. We emphasize that non-spin-polarized GGA or LDA leads to a metallic character for  $\text{UO}_2$ , which prevents us from considering charged defects.

## 4. Point defects in uranium dioxide

Point defects are modelled in a supercell containing either 24 atoms (i.e. two cubic cells of the  $\text{UO}_2$  lattice) or 12 atoms (i.e. one cubic cell of the cubic  $\text{UO}_2$  lattice). These supercells are repeated by translation in the whole 3D space to form the infinite crystal. The point defects (interstitials and vacancies) are introduced in the supercells. For both supercells considered it is thus the proportion of defects in the system which differs. The ideal situation would be to consider very large supercells to insure that defects are not interacting. A 24 atom supercell is however the maximum which can be considered to limit the computational effort. The comparison of the results obtained for the 12 and the 24 atom supercells will give an indication on the degree of uncertainty of the results with regards to the supercell size. Total energy calculations are done for the following defects: uranium and oxygen interstitials and vacancies. For the interstitial defects, only the octahedral site (i.e. the center of the oxygen cube) is taken into account, even though Willis [21] finds by neutron diffraction that oxygen interstitials in uranium oxides with composition range  $\text{UO}_{2.00}$ – $\text{UO}_{2.25}$  are localized at strongly distorted sites compared to the center of the cube. By ab initio calculations in the LDA, Crocombette et al. [2] however obtained that the octahedral sites were indeed the most stable for oxygen interstitials.

The energies of formation of these single point defects enable to calculate the formation energies of complex defects: Frenkel pairs, which consist of a vacancy and an interstitial of the same chemical type, and Schottky defects, which consist of two oxygen vacancies and one uranium vacancy. The vacancies and the interstitials forming a Frenkel pair or a Schottky defect are assumed to be dissociated and at a sufficient distance from each other so that they are non-interacting.

### 4.1. Volume variation in $\text{UO}_2$

For each type of vacancies and interstitials, and for both the 12 and 24 atom supercells, the position of the atoms and the volume of the supercell are optimized to minimize the stress and get the equilibrium structure. The volume variation induced by the defects are reported in Table 4: the absolute volume variation  $\Delta V$  of the supercell relative to the volume of the supercell

Table 3  
Equilibrium volume ( $V_o$  in a.u.<sup>3</sup>), bulk modulus ( $B_o$  in GPa) and cohesive energy ( $E_{co}$  in eV) of  $\text{UO}_2$  in the LDA [2] and the GGA, and comparison to experimental data

	$V_o$ (a.u. <sup>3</sup> )			$B_o$ (GPa)			$E_{co}$ (eV)	
	LDA	GGA	Experimental	LDA	GGA	Experimental	GGA	Experimental
$\text{UO}_2$	243	266	276	252	194	207	24.6	22.0

Table 4

Volume variation of  $\text{UO}_2$  induced by uranium and oxygen vacancies (Vac) and interstitials (Int): absolute variation  $\Delta V$  (in a.u.<sup>3</sup>) and relative variation  $\Delta V/V$  (in %) of the supercell volume, and variation  $\Delta V/V_o$  (in %) relative to the elementary volume  $V_o$  of  $\text{UO}_2$ . The results are obtained in the GGA for a 12 and a 24 atom supercell

Volume variation		U-Vac	O-Vac	U-Int	O-Int
12 atoms	$\Delta V$ (a.u. <sup>3</sup> )	−88	5	146	8
	$\Delta V/V$ (%)	−8	1	14	1
	$\Delta V/V_o$ (%)	−33	2	55	3
24 atoms	$\Delta V$ (a.u. <sup>3</sup> )	−82	49	149	18
	$\Delta V/V$ (%)	−4	2	7	1
	$\Delta V/V_o$ (%)	−31	18	56	7

without defect, the corresponding relative variation  $\Delta V/V$ , as well as the variation  $\Delta V/V_o$  relative to the elementary volume  $V_o$  of uranium dioxide (266.0 a.u.<sup>3</sup>).

We see that the volume variation is the largest for uranium interstitials which cause a swelling of around 150 a.u.<sup>3</sup> of the crystal. Besides, only uranium vacancies also induce a sensitive variation of the volume, but smaller and negative. Oxygen defects do not cause any important variation. One however sees that oxygen vacancies cause a swelling of the crystal, which can be attributed to charge repulsion between the uranium cations unshielded by the missing anion.

The values obtained for the relative variation  $\Delta V/V_o$  gives an information on the convergence of the size of the supercell to model non-interacting defects: if the size of the supercell is too small, a point defect can interact with the point defects of the adjacent supercells.  $\Delta V/V_o$  should converge to an asymptotic limit with the size of the supercell. The volume variation  $\Delta V/V_o$  obtained for both the 12 and 24 atom supercells are almost similar, proving that a 24 atom supercell is enough to have non-interacting point defects, except however in the case of the oxygen vacancies.

#### 4.2. Formation energies of point defects in $\text{UO}_2$

The formation energies  $E_{V_X}^F$  and  $E_{I_X}^F$  of a vacancy ( $V_X$ ) or an interstitial ( $I_X$ ) of the  $X$  chemical specie are

obtained from the total energies of the system with and without the defect, at constant volume, according to:

$$E_{V_X, I_X}^F = E_{V_X, I_X}^{N \mp 1} - E^N \pm E_X, \quad (3)$$

where  $E_{V_X, I_X}^{N \mp 1}$  is the calculated total energy of the supercell with the defect (and relaxed atomic positions within the supercell),  $E^N$  is the calculated total energy of the supercell without defect, and  $E_X$  is the calculated energy of the  $X$  element in the chosen reference state (the  $\alpha$ -U crystal for U defects and a  $\text{O}_2$  molecule for O defects). The formation energy of a Frenkel pair of the  $X$  specie (FP $_X$ ) is given by

$$E_{\text{FP}_X}^F = E_{V_X}^{N-1} + E_{I_X}^{N+1} - 2E^N \quad (4)$$

and for the Schottky defect ( $S$ ) by

$$E_S^F = E_{V_U}^{N-1} + 2E_{V_O}^{N-1} - 3\frac{N-1}{N}E^N \quad (5)$$

with  $N$  the number of atoms in the defect-free supercell. The formation energies of the defects obtained are reported in Table 5, for the 12 and the 24 atom supercells. They are compared to the previous theoretical results: the ab initio results by Crocombette et al. [2] and by Petit et al. [1] both in the LDA and for a 24 atom supercell, and the results by Jackson et al. [22] in the semi-empirical Mott–Littleton approach. The values obtained by Matzke [23] from diffusion measurements for Schottky defects and Frenkel pairs are also given.

We first see that the values obtained with the GGA formation energies for the 12 atom supercell and those obtained for the 24 atom supercell are not very different: the difference amounts to 7% at most. The formation energies of defects for a 24 atom supercell are thus already quite converged as a function of the supercell size. On the other hand, the difference in the formation energy is much larger if we compare the GGA and the LDA values of Crocombette et al. [2] for the 24 atom supercell: a 30% difference is obtained for the uranium vacancies which are found less stable with the GGA. As a consequence, the uranium Frenkel pairs are also found less stable than in the LDA. However, in both the GGA and the LDA, the calculated formation energies of Frenkel pairs and Schottky defects are in the

Table 5

Formation energies (eV) of point defects in  $\text{UO}_2$ : uranium and oxygen vacancies (U-Vac and O-Vac), uranium and oxygen interstitials (U-Int and O-Int), Frenkel pairs (O-FP and U-FP), and Schottky defect ( $S$ )

Formation energy (eV)	U-Vac	O-Vac	U-Int	O-Int	O-FP	U-FP	$S$
GGA 12 atoms	5.1	6.1	7.5	−2.6	3.5	12.6	6.0
GGA 24 atoms	4.8	6.1	7.0	−2.5	3.6	11.8	5.6
LDA 24 atoms [2]	3.3	6.7	7.3	−2.9	3.9	10.7	5.8
LDA-LMTO [1]	19.1	10.0	11.5	−3.3	6.7	30.6	17.1
Semi-empirical [22]	80.2	16.9	−60.8	−12.1	4.8	19.4	11.3
Matzke [23]	–	–	–	–	3.0–4.6	9.5	6.0–7.0

range of the experimental values, only the formation energy of uranium Frenkel pairs seems over-estimated by the calculations. A discussion on the comparison to the LMTO-ASA values of Petit et al. [1] and to the semi-empirical ones of Jackson et al. [22] can be found in Ref [2]. In any case, all ab initio results agree on predicting the larger stability of oxygen Frenkel pairs over uranium Frenkel pairs and Schottky defects. Furthermore, the negative sign for the formation energy of oxygen interstitials predicts the instability of  $\text{UO}_2$  in presence of oxygen vapor, the incorporation of oxygen atoms occurring at the interstitial site of the crystal. This agrees with the well-known first step of the oxidation mechanism of  $\text{UO}_2$ .

#### 4.3. Variation of the defect concentrations with the stoichiometry in $\text{UO}_2$

The point defect model (PDM) [23,24] is a thermodynamical model linking the defect concentrations to the defect formation energies. In this model, the point defects are assumed non-interacting and at thermodynamical

equilibrium. In the so-called closed regime (in which the system cannot exchange atoms with the exterior), the set of equations linking the equilibrium defect concentrations to the formation energies is given as follows:

$$[V_{\text{O}}][I_{\text{O}}] = \exp\left(-\frac{E_{\text{FP}_{\text{O}}}^{\text{F}}}{k_{\text{B}}T}\right), \quad (6)$$

$$[V_{\text{U}}][I_{\text{U}}] = \exp\left(-\frac{E_{\text{FP}_{\text{U}}}^{\text{F}}}{k_{\text{B}}T}\right), \quad (7)$$

$$[V_{\text{O}}]^2[V_{\text{U}}] = \exp\left(-\frac{E_{\text{S}}^{\text{F}}}{k_{\text{B}}T}\right), \quad (8)$$

$$2[V_{\text{U}}] + [I_{\text{O}}] = 2[I_{\text{U}}] + 2[V_{\text{O}}] + x, \quad (9)$$

where  $x$  is the deviation from stoichiometry in uranium dioxide  $\text{UO}_{2+x}$ ,  $[V_{\text{O}}]$ ,  $[V_{\text{U}}]$ ,  $[I_{\text{O}}]$  and  $[I_{\text{U}}]$  are the concentrations of oxygen and uranium vacancies and of oxygen and uranium interstitials respectively, and  $E_{\text{FP}_{\text{O}}}^{\text{F}}$ ,  $E_{\text{FP}_{\text{U}}}^{\text{F}}$ ,  $E_{\text{S}}^{\text{F}}$  are the formation energies of oxygen and uranium Frenkel pairs and of a Schottky defect. Point defect concentrations are defined in a lattice model as the number

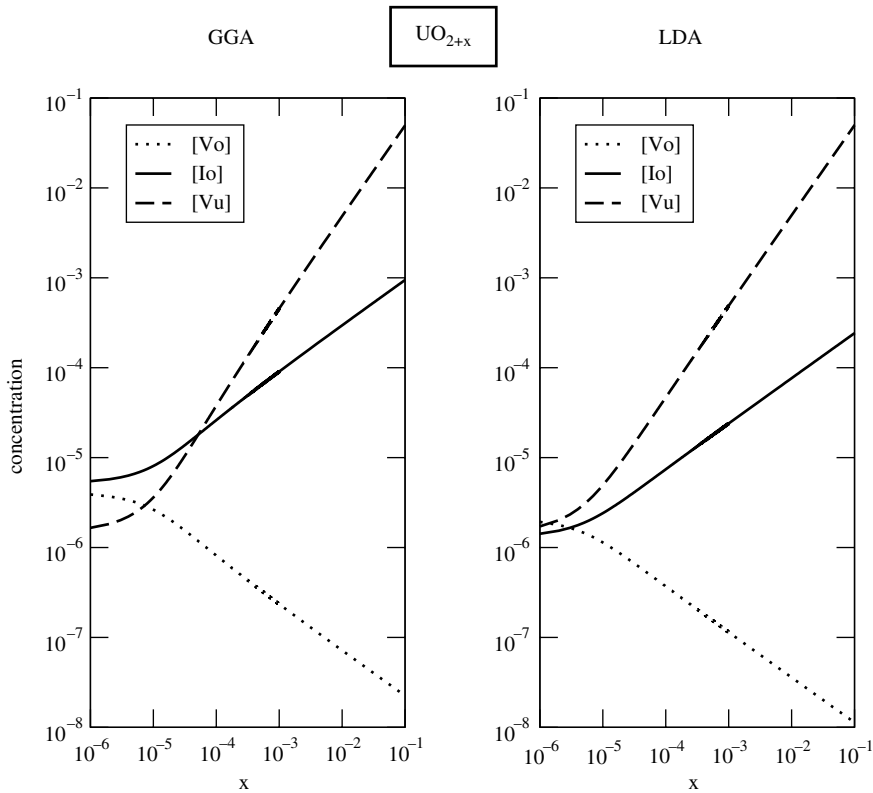


Fig. 2. Variation of the point defect concentrations in  $\text{UO}_{2+x}$  with the deviation from stoichiometry  $x$ , according to the point defect model with a temperature of 1700 K. The formation energies of the defects used are those obtained by our ab initio calculations: on the left panel, the ab initio calculations were performed with the GGA formation energies, on the right panel with the LDA formation energies [2]. The variation of concentration is represented for U and O vacancies ( $V_{\text{U}}$  and  $V_{\text{O}}$ ) and O interstitials ( $I_{\text{O}}$ ). The concentration of uranium interstitials is negligible and thus not shown.

of defects present divided by the number of available sites for the defect under consideration. A point to be kept in mind arises for oxygen vacancies. For this defect, there are two possible sites in each unit cell which are the two positions occupied by the oxygen atoms in the defect free crystal. All other defects have only one possible site per unit cell, the uranium site for the uranium vacancy and the center of an oxygen cube for the interstitials. Hence, in a crystal where there are as many oxygen vacancies as oxygen interstitials, the concentration of oxygen vacancies is two times smaller than the one of interstitials.

By solving the set of equations using the formation energies previously calculated (Table 5), one can determine the evolution of the defect concentrations as a function of the deviation from stoichiometry  $x$ . An arbitrary temperature  $T$  of 1700 K was chosen.

#### 4.3.1. Hyper-stoichiometric $UO_{2+x}$

Figs. 2 and 3 show the evolution of the defect concentrations using the two sets of formation energies obtained in either the LDA or the GGA for a 24 atom supercell.

The hyper-stoichiometric case  $UO_{2+x}$ , which would correspond to oxidized uranium dioxide, is shown first (Fig. 2). The hypo-stoichiometric case  $UO_{2-x}$  is discussed in the following subsection.

Although the formation energies obtained in the LDA and in the GGA for the Frenkel pairs and the Schottky defect are of the same order of magnitude, they yield a different behavior for the evolution of the defect concentrations as a function of  $x$ . The main difference is to be seen for small values of  $x$  ( $x$  smaller than  $10^{-4}$ ), i.e. close to stoichiometry: with the GGA formation energies, the concentration of oxygen interstitials is the largest, whereas with the LDA formation energies it is the concentration of uranium vacancies which is always the largest whatever the value of  $x$ .

This disagreement is a consequence of the condition of application of the PDM: to ensure that the PDM reproduces the fact that oxygen defects are dominant for all stoichiometries, the condition  $E_{FPo}^F/2 \leq E_{FPu}^F/3$  should be fulfilled. It is not fulfilled by the LDA formation energies, but it is indeed by the GGA ones (see Ref. [2]).

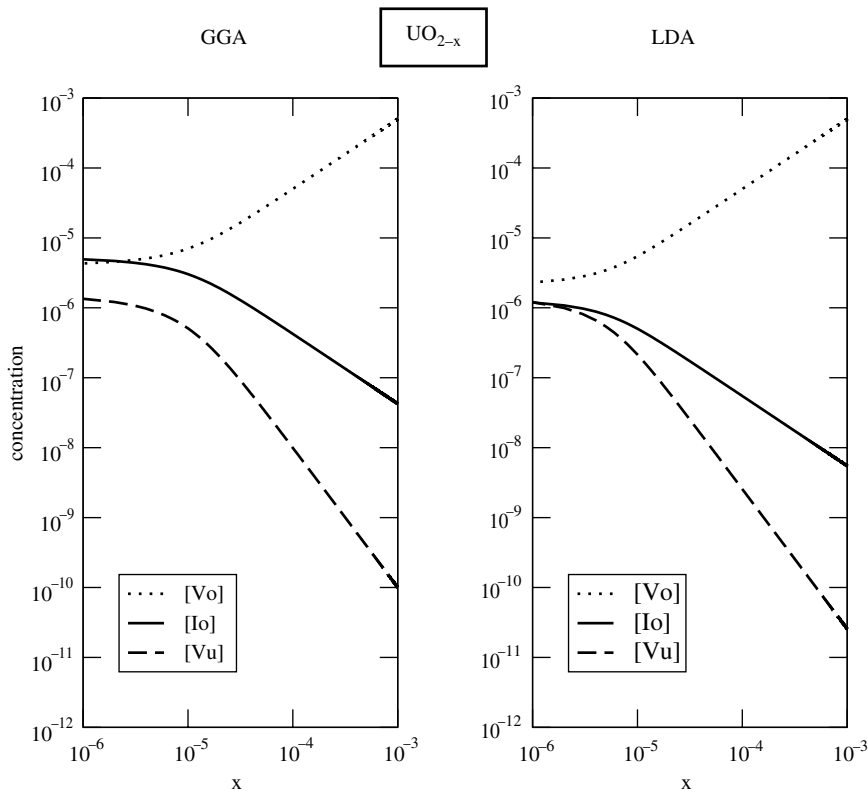


Fig. 3. Variation of the point defect concentrations in  $UO_{2-x}$  with the deviation from stoichiometry  $x$ , according to the point defect model with a temperature of 1700 K. The formation energies of the defects used are those obtained by our ab initio calculations: on the left panel, the ab initio calculations were performed with the GGA formation energies, on the right panel with the LDA formation energies [2]. The variation of concentration is represented for U and O vacancies ( $V_U$  and  $V_O$ ) and O interstitials ( $I_O$ ). The concentration of uranium interstitials is negligible and thus not shown.

For larger deviations  $x$  from stoichiometry, both the LDA and the GGA set of formation energies give the uranium vacancies as the defects with the highest concentration. It is however experimentally known that oxygen defects dominate over uranium defects, and in particular that hyper-stoichiometry is accommodated by oxygen interstitials, leaving the uranium sublattice roughly undisturbed [21]. This discrepancy can be attributed to the limits of the PDM which assumes isolated non-interacting defects, whereas for large deviations from stoichiometry, the many oxygen interstitial defects are known to form clusters [3]. The formation of such oxygen clusters is not taken into account by the present model nor by the ab initio calculations. This thus leads for large deviations from stoichiometry to an erroneous description of the oxygen concentration defects, and to a dominating uranium vacancy concentration.

#### 4.3.2. Hypo-stoichiometric $UO_{2-x}$

In a similar way, the evolution of the defect concentrations is determined in the hypo-stoichiometric case according to the PDM (Fig. 3). One sees that in hypo-stoichiometric uranium dioxide  $UO_{2-x}$ , both the GGA and the LDA sets of formation energies yield similar behavior for the variation of the defect concentrations: the larger the deviation from stoichiometry  $x$  is, and the larger the oxygen vacancy concentration is, as could be expected.

## 5. Conclusion

We show that the generalized gradient approximation (GGA) for exchange–correlation within the density functional theory (DFT) gives good results for the ground-state properties of uranium and uranium dioxide, and thus yields reliable values for the formation energies of point defects in  $UO_2$ . Vacancies, interstitials, Frenkel pairs and Schottky defects are considered. Oxygen interstitials are found to have a negative formation energy with regard to gaseous oxygen, confirming the easy oxidation of  $UO_2$  and the first step of the oxidation mechanism by oxygen incorporation at an interstitial site. Using these GGA formation energies, the thermodynamical point defect model (PDM) gives oxygen interstitials as the defects with the highest concentration, provided that the deviation from stoichiometry  $x$  in

$UO_{2+x}$  is small. For larger deviations from stoichiometry, the PDM, used to analyze the evolution of the defect concentrations as a function of the stoichiometry, is inappropriate since it cannot account for the formation of oxygen clusters in  $UO_2$ .

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