



# Ab initio energetics of some fission products (Kr, I, Cs, Sr and He) in uranium dioxide

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## Abstract

A computational study of some fission products (FP) energetics in uranium dioxide is presented. Krypton, iodine, caesium, strontium and helium are considered. Calculations are made within the density functional theory in the local density approximation with the plane wave pseudopotential method. Three insertion sites are considered: the octahedral interstitial position and the oxygen and uranium substitution sites. The importance of atomic relaxations is estimated on the He and Kr cases. They prove quantitatively important but can be neglected to draw qualitative trends. For each fission product incorporation and solution energies are calculated. The obtained values of the solution energies of the various FP are in good agreement with their experimental behaviour: Kr, Cs and I atoms are insoluble in uranium dioxide, Sr solubility depends on the stoichiometry of uranium. He atoms are found to have little interaction with their environment in uranium dioxide.

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## 1. Introduction

Lattice sites and solution energies of fission products (FP) are of major importance in fundamental studies of nuclear fuels. They pilot the dependence of the behaviour of FP on fuel stoichiometry and temperature, as well as their possible release from the fuel in the context of a direct storage of spent fuel. As experimental studies in this field are very difficult, computational works are of great value. This paper presents results on some FP energetics in mono-crystalline uranium dioxide used as a model of nuclear fuel. The present study deals with five FP: Kr, I, Cs, Sr and He. The first four FP are important in the context of direct disposal. Krypton atoms form bubbles that may alter the structural and mechanical properties of the fuel (see [1] and references therein); iodine and caesium have long life isotopes ( $^{139}\text{I}$  and

$^{135}\text{Cs}$ ) and are known to be highly dissoluble in water and to have a high instant release fraction [2]; Sr is considered as a tracer for spent fuel dissolution [3]. Strictly speaking, He is not a fission product as it is only marginally produced during fuel burn-up. Therefore its influence has long been neglected. Nevertheless it will be produced in nonnegligible amounts during storage by actinides  $\alpha$ -disintegrations, especially in MOX fuels.

Most of the previous computational works employed empirical potentials (EP) [4–10] to calculate the energies of FP in  $\text{UO}_2$  (for a thorough theoretical study and a detailed comparison with experiments see [7]). Some studies included the use of quantum mechanical based calculations to describe the immediate neighbouring of the FP [5,6]. To our knowledge, only one modern density functional theory (DFT) modelling study has been published on the incorporation of Kr atoms [11]. In that study, the linear Muffin tin orbital method in the atomic sphere approximation (LMTO-ASA) was used in the framework of the local density approximation (LDA). The present work deals with FP in uranium dioxide in

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the same framework using the plane wave pseudopotential approach which is known to give very accurate results for point defects studies or dopants [12–15]. This paper comes after a previous study [16] on uranium dioxide point defects in which the same theoretical method and especially the same pseudopotentials for uranium and oxygen were used. Values of the formation energies of the intrinsic point defects are taken from that study.

## 2. Calculations

### 2.1. *Ab initio* technique

Technicalities of the calculations are, on the whole, the same than in our previous paper on point defects [16]. They are only briefly recalled in the following. Calculations are carried out in the DFT-LDA framework. The exchange and correlation functional is of the Perdew–Zunger type [17]. We use the plane wave self-consistent field [18] which deals with a plane wave basis and uses pseudopotentials [19]. As it happens for any calculations made in local density or generalised gradient approximations [20–24] a metallic state is obtained for  $\text{UO}_2$  while it is experimentally an insulator. This inability to reproduce the insulating nature of  $\text{UO}_2$  is due to an inaccurate description of electronic correlations and especially of the localised character of uranium  $f$  electrons. Nevertheless the structural characteristics of  $\text{UO}_2$  are correctly reproduced. Indeed an equilibrium unit cell parameter of 5.24 Å and a bulk modulus of 252 GPa are obtained in overall agreement with the experimental values of 5.47 Å and 207 GPa for the unit cell parameter and the bulk modulus respectively.

To study the insertion of FP, the supercell method is employed. The supercell, cut-off energy and  $k$  point sampling are the same than in [16] to which the reader can refer for a discussion about the convergence of the results with these parameters. Due to computer limitations we have to restrict to a defect free 24 atoms su-

percell made of the repetition, over one of the three axes, of the 12 atom conventional unit cell of uranium dioxide. The unit cell parameter of this conventional cell has been fixed to 5.24 Å which is the calculated equilibrium value for bulk uranium. An energy cut-off of 120 Ry was chosen. Six  $k$  points are used to sample the irreducible Brillouin zone of the supercell. The imprecision on total energies due to the limitations in cut-off energy, supercell size and  $k$  point sampling should not be larger than 0.1 eV. The pseudopotentials used in the calculations to represent the different kind of atoms are indicated in Table 1.

Only three simple insertion sites were considered: a fission product is inserted either in an interstitial octahedral site or in substitution for an oxygen or an uranium atom. The energy of boxes containing either an oxygen or an uranium vacancy that enter the definitions of the relevant thermodynamical quantities (see below) are taken from the previous study on point defects in [16].

### 2.2. Thermodynamic quantities

In this section the thermodynamic quantities used to examine the solution of FP and their relation with the calculated energies of the boxes are defined. In the following one deals only with internal energies thus neglecting entropy terms. First, to determine the stability of FP trapped in pre-existing sites and compare them, one should calculate the incorporation energies of the different insertion sites. The incorporation energy of a fission product in a specific site  $E_{\text{PF,SX}}^{\text{inc}}$  is defined as the energy needed to insert the FP in a pre-existing trap site. It is obtained from the calculated energies of the boxes with and without the fission product:

$$E_{\text{PF,SX}}^{\text{inc}} = E_{\text{PF,SX}} - E_{\text{SX}} - E_{\text{PF}}^{\text{isolated}}. \quad (1)$$

In this expression  $E_{\text{PF,SX}}$  is the energy of the cell containing the fission product in site X;  $E_{\text{SX}}$  is the energy of

Table 1  
Type of pseudopotentials used to represent the elements

	Element						
	U	O	He	Kr	I	Cs	Sr
Pseudopotential type	TM	TM	TM	TM	HGH	HGH	HGH
Valence	6s <sup>2</sup> (1.26)	2s <sup>2</sup> (1.45)	1s <sup>2</sup> (1.0)	4s <sup>2</sup> (1.7)	Valence	Semi-core	Semi-core
	6p <sup>6</sup> (1.52)	2p <sup>4</sup> (1.45)		4p <sup>6</sup> (1.7)			
	6d <sup>1</sup> (2.20)						
	5f <sup>3</sup> (1.26)						

The second line indicates the pseudopotentials type: TM stands for Trouillier–Martins [30], HGH stands for Hartwigsen–Goedecker–Hutter [31]. The third line provides details about the valence configurations. For TM pseudopotentials, the valence states and the associated core radii (in a.u.) in brackets are indicated. For HGH pseudopotentials one indicates which type has been chosen in the table of Ref. [31].

the cell containing an empty site of type X;  $E_{PF}^{\text{isolated}}$  is the energy of an isolated atom of FP. It is estimated by placing a single atom of FP in an empty cell.

A positive result means that energy is required to incorporate the FP in the solid, whereas a negative energy implies that incorporation is energetically favourable. The use of incorporation energy is limited since it is not sensitive to any equilibrium between trap sites. Nevertheless it can be used to predict the most stable trap sites for FP provided that trap sites are equivalently available for occupations. Incorporation energies therefore may give an insight of what happens in the fuel at very low burn-up. In this situation, the concentration of FP are still very small and the population of trap sites are much higher than at thermal equilibrium because of the defects produced by irradiation. However, applying standard equilibrium thermodynamics to an under irradiation situation remains questionable.

To take into account the equilibrium between the different trap sites one should consider solution energies. For a certain FP and a certain site X, the solution energy,  $E_{PF,SX}^{\text{sol}}$ , is defined as the incorporation energy of the FP in the site plus the apparent (see below) formation energy of the trap. It is clear that for an interstitial site, incorporation and solution energies are equal. For vacancy insertion sites one has

$$E_{PF,SX}^{\text{sol}} = E_{PF,SX}^{\text{inc}} + E_{V_X}^{\text{Fapp}}, \quad (2)$$

where  $E_{V_X}^{\text{Fapp}}$  is the apparent formation energy of the vacancy site.

Solution energies should be used to express the populations of FP in the different sites when complete thermodynamical equilibrium is achieved for FP and for trap sites. Solution energies depend on fuel stoichiometry through the variation of the apparent vacancy formation energies with stoichiometry which, for a given temperature, stoichiometry and vacancy type  $V_X$  is defined by

$$E_{V_X}^{\text{Fapp}} = -kT \ln([V_X]). \quad (3)$$

Apparent formation energies can be expressed in the framework of the point defect model introduced by Matzke [25] and Lidiard [26] to formalise the populations of defects in uranium dioxide and their variations with stoichiometry. They depend on the oxygen Frenkel

Table 2  
Formation energies of uranium dioxide intrinsic point defect taken from [16] (in eV)

Formation energies	$E_{FPo}^F$	$E_S^F$
Relaxed	3.9	5.8
Unrelaxed	3.9	7.5

The relaxed and unrelaxed values are indicated.  $E_{FPo}^F$  and  $E_S^F$  are the oxygen Frenkel pair and Schottky defect formation energies.

(vacancy–interstitial) pair and Schottky defect formation energies (a Schottky defect is made of one uranium and two oxygen disconnected vacancies). Values of the formation energies, taken from [16], are given in Table 2. The equations of the point defect model are recalled in Appendix A. They lead to the apparent formation energies given in Table 3.

### 3. Effect of atomic relaxation: test on He and Kr

Plane wave formalism allows the calculation of atomic relaxation. Starting from perfect crystalline sites, the atomic positions can be relaxed step by step to their local minimum. Such relaxed calculations are much more demanding in computer time than the unrelaxed ones as series of atomic positions should be considered. To be consistent, one should take into account atomic relaxation for all steps of the calculations or, at the opposite, neglect them at all steps. Thus, for the incorporation energies, that means that one should consider either unrelaxed or relaxed values for both  $E_{PF,SX}$  and  $E_{SX}$ . For solution energies the apparent formation energies of the sites are different when one does or does not take into account relaxation (see Table 2).

The importance of atomic relaxation is assessed on the helium and krypton cases. In Table 4 relaxed and unrelaxed values of incorporation and solutions energies of He and Kr atoms in stoichiometric  $UO_2$  (at zero temperature) are compared. For helium atoms the effect of relaxation is very small for both incorporation and solution energies except for the solution energy in an uranium site. The small effect of relaxation on helium incorporation energies comes from the fact that the introduction of an helium atom in  $UO_2$  does not change

Table 3

Expressions of the apparent formation energies of oxygen ( $E_{VO}^{\text{Fapp}}$ ) and uranium ( $E_{VU}^{\text{Fapp}}$ ) vacancy sites as function of temperature ( $T$ ) and deviation from stoichiometry ( $x$ ) in  $UO_{2+x}$

Stoichiometry	$x < 0$	$x = 0$	$x > 0$
$E_{VO}^{\text{Fapp}}$	$-kT \ln(-x/2)$	$\frac{E_{FPo}^F}{2} + kT \ln(2)$	$E_{FPo}^F + kT \ln(x)$
$E_{VU}^{\text{Fapp}}$	$E_S^F + 2kT \ln(-x/2)$	$E_S^F - E_{FPo}^F - kT \ln(2)$	$E_S^F - 2E_{FPo}^F - 2kT \ln(x)$

$E_{FPo}^F$  and  $E_S^F$  are the oxygen Frenkel pair and Schottky defect formation energies.

Table 4

Incorporation energy and solution energy in stoichiometric  $\text{UO}_2$  of He and Kr atoms (in eV): comparison of relaxed and unrelaxed calculations

	$E_{\text{inc}}$		$E_{\text{sol}} x = 0$	
	Unrelaxed	Relaxed	Unrelaxed	Relaxed
He–O	1.8	1.7	3.7	3.6
He–U	0.2	0.1	3.8	2.0
He octa	1.3	1.3	1.3	1.3
Kr–O	10.0	7.1	11.9	9.0
Kr–U	5.1	4.0	8.7	6.0
Kr octa	10.6	8.9	10.6	8.9

PF-X stands for the fission product FP in site X.

the atomic configuration of the insertion site. This is probably due to the small size of He atoms and to the weakness of chemical interactions between He and its neighbours. For what concerns He solution energies, the uranium vacancy site is the only one affected as relaxation is important only for uranium defects (see Table 2 and Ref. [16]). For krypton atoms the discrepancy between relaxed and unrelaxed calculations ranges between 1.0 and 3.0 eV. Energies associated to krypton atoms are all affected by relaxation due to the large size of Kr atoms. Introducing a Kr atom thus induces quite important atomic rearrangements.

The quantitative importance of atomic relaxation is therefore nonnegligible, the imprecision associated with the use of unrelaxed configurations being of the order of 2 eV. Nevertheless, comparing, for a given FP, the different insertion sites, one can see that their respective order is nearly always the same for unrelaxed and relaxed calculations. Moreover the respective orders of the solution and incorporations energies for He and Kr atoms are the same for relaxed and unrelaxed calculations. To draw general trends and compare qualitatively different FP, it therefore proves sufficient to deal with unrelaxed calculations. This is what we chose to do for the other FP considered in this study (I, Cs, Sr). Except where otherwise stated, all the following discussion deals with unrelaxed configuration figures, including for He and Kr.

## 4. Results

### 4.1. Incorporation energies

Calculated values of the incorporation energies of He, Kr, Cs, I and Sr atoms are given in Table 5. For comparison the values obtained with EP as given in [7] are also indicated. The calculations that included some quantum mechanical treatment of the FP immediate

Table 5

Incorporation energies of empirical potentials (EP) in uranium dioxide (in eV)

Incorporation energies	Present work (PW-PP)	EP
He–O	1.8	–0.1
He–U	<i>0.2</i>	0.0
He octa	1.3	–0.1
Kr–O	10.0	9.9
Kr–U	<i>5.1</i>	3.2
Kr octa	10.6	13.3
Cs–O	17.9	9.1
Cs–U	<i>3.6</i>	–6.7
Cs octa	15.0	9.9
I–O	14.8	8.9
I–U	<i>4.1</i>	8.8
I octa	13.2	15.8
Sr–O	9.2	–8.9
Sr–U	<i>–6.4</i>	–27.7
Sr octa	6.9	–11.0

The results of the present work are given for unrelaxed configurations. PF-X stands for the fission product (FP) in site X. EP results are taken from [7]. For each FP and method, the minimum is indicated in italics.

Table 6

Incorporation and solution energies of Kr atoms calculated with the LMTO-ASA method (in eV); results from [11]

	$E_{\text{inc}}$	$x < 0$	$x = 0$	$x > 0$
Kr–O	8.0	<i>8.0</i>	<i>11.4</i>	14.7
Kr–U	<i>3.0</i>	20.4	13.4	<i>6.7</i>
Kr octa	14.2	14.2	14.2	14.2

For each stoichiometry, the minimum is indicated in italics.

surrounding gave results within 0.2 eV of ionic potentials calculations [5,6]. LMTO-ASA results [11] for Kr are summarised in Table 6. One can see that for all FP, the incorporation energy is minimum for the uranium vacancy site. For I, Cs and Sr atoms the incorporation energies in the uranium vacancy site are around 10 eV below the energy calculated for the other sites. Rare gases incorporations energies are closer to each other. This is especially true for He.

For Kr, I and Cs atoms large positive incorporation energies are obtained which means that, whatever the number of available insertion sites may be, the introduction of these FP in  $\text{UO}_2$  is largely penalised energetically. At the opposite, it is energetically favourable to incorporate a Sr atom in an available uranium vacancy. Finally, He atoms seem to have little interaction with their environment in  $\text{UO}_2$  as indicated by the small absolute values of their incorporation energies.

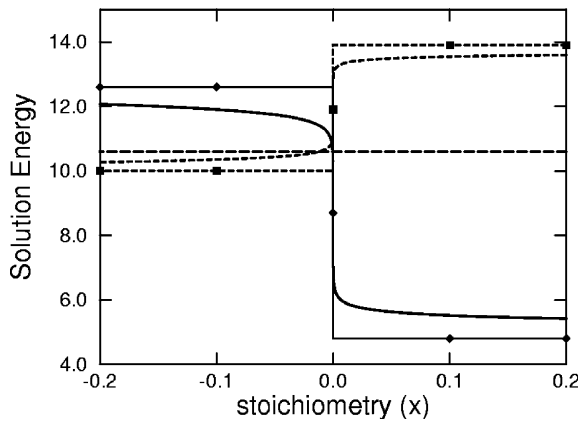


Fig. 1. Variation of the solution energy with the deviation from stoichiometry ( $x$ ) in  $\text{UO}_{2+x}$ , example of Kr at  $T = 1400$  K. Uranium site: solid lines; interstitial site: dashed line; oxygen site: dotted lines. The curved lines follow the formulas of Table 3 for the site apparent formation energies of the vacancy sites. The neglect of temperature dependent terms in these formulas leads to the straight lines and symbols for the uranium (solid line and diamond symbol) and oxygen (dotted line and square symbol) insertion sites.

#### 4.2. Solution energies

The variation of the solution energies of FP with stoichiometry are exemplified in Fig. 1 with the case of Kr for an arbitrary temperature of 1400 K. Fig. 1 stresses the very fast variation of these solution energies with stoichiometry in the nearly stoichiometric regime. For larger deviation from stoichiometry the variation of the solution energies is smaller. Similar graphs could be drawn for all FP. However a simplified way to present the results for the solution energies has been used in former papers. It is based on the neglect of the variation of the apparent formation energies with temperature that appears in the equations of Table 3. One then considers only the three limiting cases of under-, perfect and over-stoichiometry. Each curve reduces to two horizontal half line for under- and over-stoichiometry and one point on the  $x = 0$  axis for perfectly stoichiometric oxide (see the example in Fig. 1). This simplified presentation allows one to deal with figures instead of graphs. We followed this procedure to present our results in Table 7 and compare them with former published calculations. To get the solution energies for the LMTO-ASA calculations (Table 6) point defect formation energies from [27] are used.

For I, Cs and Sr atoms the difference between incorporation energy in the uranium vacancy site and in the other sites is large enough to counteract the large apparent formation energy of uranium vacancies and to favour the uranium solution site for all stoichiometries. At the opposite for rare gases, the lowest energy solution

Table 7

Solution energies of empirical potentials (EP) in under-, perfectly and over-stoichiometric uranium dioxide

$E_{\text{sol}}$	Present work			EP		
	$x < 0$	$x = 0$	$x > 0$	$x < 0$	$x = 0$	$x > 0$
He–O	1.8	3.7	5.7	–0.1	3.4	6.8
He–U	7.7	3.8	–0.1	13.9	7.0	0.2
He octa	<i>1.3</i>	<i>1.3</i>	1.3	–0.1	–0.1	–0.1
Kr–O	<i>10.0</i>	11.9	13.9	9.9	13.3	16.8
Kr–U	12.6	8.7	4.8	17.2	<i>10.3</i>	3.5
Kr octa	10.6	10.6	10.6	13.3	13.3	13.3
Cs–O	17.9	19.8	21.8	9.1	12.5	15.9
Cs–U	<i>11.1</i>	7.2	3.3	7.3	<i>0.4</i>	–6.4
Cs octa	15.0	15.0	15.0	9.9	9.9	9.9
I–O	14.8	16.7	18.7	8.9	<i>12.3</i>	15.8
I–U	<i>11.6</i>	7.7	3.8	22.1	15.3	8.5
I octa	13.2	13.2	13.2	15.8	15.8	15.8
Sr–O	9.2	11.1	13.1	–8.9	–5.5	–2.1
Sr–U	<i>1.1</i>	–2.8	–6.7	–13.8	–20.6	–27.4
Sr octa	6.9	6.9	6.9	–11.0	–11.0	–11.0

The results of the present work are given for unrelaxed configurations. FP-X stands for the fission product (FP) in site X. EP results are taken from [7]. For each stoichiometry, FP and method, the minimum is indicated in italics.

site, i.e. the thermodynamically favoured solution site depends on stoichiometry. Thus in the Kr case the solution site goes from oxygen to uranium vacancy site passing from under-stoichiometry to stoichiometry. For He atom, the solution site is the interstitial position for the under-stoichiometric and stoichiometric oxide and turns to the uranium vacancy for over-stoichiometry only.

For all stoichiometries one gets quite large and positive solution energies for Kr, I and Cs atoms. Thus at thermal equilibrium the concentration of these fission product in  $\text{UO}_2$  should be negligible for all stoichiometries.

## 5. Discussion

### 5.1. Comparison with former calculations

First, one can note that FP are found to preferentially insert in uranium sites which are the largest considered sites. Based on this observation, one could imagine considering larger sites made of assemblies of two or three vacancies. To exist at equilibrium such complex sites should have large binding energies to counteract the loss of configurational entropy of associated vacancies with regards to dissociated defects. Former LMTO-ASA calculations on Kr by Petit et al. [11] predicted that the associated Schottky trio (three

connected vacancies) gives the lowest incorporation energy, but not the lowest solution energy. With EP [7] it was found that such complex sites may even give the lowest solution energies for some FP especially in the under-stoichiometric regime. However, even if such complex sites are neglected in the present work, PW-PP results are, on the whole, in agreement with what is obtained with EP or the LMTO-ASA method. Focusing on each FP separately, the most stable pre-existing trap site, indicated by the lowest incorporation energy, is the same for the three calculation methods. Taking into account the equilibrium between trap sites (using the solution energies) also lead to nearly identical site predictions for the three methods.

Quantitatively, calculated solution energies with LMTO-ASA and PW-PP are within 2 eV of each other apart for Kr atoms in stoichiometric  $\text{UO}_2$  for which a different solution site is predicted. Differences of that order of magnitude are not uncommon in *ab initio* calculations and are believed to come from a difficulty of the LMTO-ASA method to deal with point defects and especially with vacancies. Indeed most of the differences between the two calculations originates in large differences in the vacancies formation energies calculated with PW [16] and LMTO-ASA [27].

Comparing PW-PP and EP results, one can see that numerical values of the solution and incorporation energies prove very different for the two methods, the difference in energies being as high as 20 eV in the case of Sr. The variation among the FP of the solution energies is also larger with EP than with PW-PP calculations. This leads to differences in predictions: the solution energies of Sr and Cs atoms in  $\text{UO}_2$  are under-estimated by EP compared to PW-PP results; different sites are predicted for iodine and helium in under and purely stoichiometric  $\text{UO}_2$  and the relative stability of Kr and I atoms in  $\text{UO}_2$  are different. For what concerns He atoms, the EP used by Grimes seems unable to describe its behaviour in  $\text{UO}_2$  as all insertion sites have an incorporation energy very close to zero. Some of the differences between EP and PW-PP may partly come from the fact that EP calculations take into account the atomic relaxations whereas they are neglected in our work. However they are more probably related to the use of formal charges in inter-ionic calculations. This is known to lead to an over-estimation of the intrinsic point defect formation energies by a factor 1.5–2 [28]. This quite strong imprecision in the EP calculations results in a quite large dispersion of the solution energies of the FP. Such a large dispersion slightly questions the qualitative prediction of EP.

### 5.2. Experimental trends

The calculated solution energies are in fair agreement with what is known of the behaviour of FP in  $\text{UO}_2$ , see

[1,7] and references therein. Kr, I and Cs atoms, which are known to be insoluble in  $\text{UO}_2$ , are found to have positive and quite large solution energies for all stoichiometries.

Sr is regarded as soluble in  $\text{UO}_2$ , but its solubility depends critically upon the oxygen to metal ratio, especially in under-stoichiometric oxide. PW-PP calculated solution energy reproduces very well this behaviour. Indeed a negative solution energy is found for stoichiometric and over-stoichiometric  $\text{UO}_2$ , Sr is therefore predicted as soluble for these stoichiometries. In the under-stoichiometric regime the solution energy goes from a positive value at high deviations from stoichiometry to a negative one near stoichiometry, indicating a gradual change from insolubility to solubility that our calculations show to be due to the decrease of available uranium vacancy sites.

Little is known about the behaviour of helium atoms in uranium dioxide as it is produced in negligible amount during fuel's burn-up. Small values are found for its incorporation and solution energies indicating a partial solubility of He in  $\text{UO}_2$ .

## 6. Conclusions

A theoretical study on FP incorporation and solutions energies in uranium dioxide has been presented. The calculations were done in the DFT-LDA framework using the PW-PP formalism and the supercell approach. Three simple insertion sites were considered: the octahedral interstitial position and the oxygen and uranium substitution sites. Atomic relaxations, estimated on the He and Kr cases, prove quantitatively important but can be neglected to draw qualitative trends. The comparison of the obtained incorporation and solution energies with former results from LMTO-ASA and EP calculations indicates that all kinds of calculations roughly exhibit the same trends. However, quite large differences appear for the numerical values of the energies, especially when EP and PW-PP results are compared. Our values of the solutions energies of the various FP are in good agreement with their experimental behaviour. Indeed Kr, I and Cs atoms have large positive solution energies indicating that they are insoluble in  $\text{UO}_2$  whereas the solubility of Sr atoms is found to depend on uranium stoichiometry.

This work demonstrates the ability of the PW-PP approach calculations to study the energetics of FP in  $\text{UO}_2$ . Such kind of calculations could be used to make systematic classifications and comparisons between the many FP that are present in the fuel. In order to get a more complete understanding of their behaviour in the matrix of the nuclear fuel, the same computational method could also be used to calculate FP diffusion coefficients.

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### Appendix A

The point defect model for  $\text{UO}_2$  [25,26] deals with the equilibrium of intrinsic point defects in uranium dioxide: Frenkel pairs of oxygen and uranium and the Schottky defect. Under the assumption that the defects are isolated, disconnected and non-interacting, writing the mass action laws for the reactions of formation of intrinsic defects gives

$$[V_{\text{O}}][I_{\text{O}}] = \exp\left(-\beta E_{\text{FP}_0}^{\text{F}}\right), \quad (\text{A.1})$$

$$[V_{\text{U}}][I_{\text{U}}] = \exp\left(-\beta E_{\text{FP}_0}^{\text{F}}\right), \quad (\text{A.2})$$

$$[V_{\text{O}}]^2[V_{\text{U}}] = \exp\left(-\beta E_{\text{S}}^{\text{F}}\right), \quad (\text{A.3})$$

$[V_{\text{O}}]$ ,  $[I_{\text{O}}]$ ,  $[V_{\text{U}}]$  and  $[I_{\text{U}}]$  are the concentrations of the oxygen and uranium vacancies and interstitials, defined as the number of defects in the material divided by the number of available sites for the defect under consideration.  $E_{\text{S}}^{\text{F}}$ ,  $E_{\text{FP}_0}^{\text{F}}$  and  $E_{\text{FP}_0}^{\text{F}}$  are the formation energies of the Schottky defect, the oxygen and the uranium Frenkel pair respectively.

A supplementary equation is given by the definition of stoichiometry in  $\text{UO}_{2+x}$ . A first order counting of the number of atoms on each site gives

$$2[V_{\text{U}}] + [I_{\text{O}}] = 2[I_{\text{U}}] + 2[V_{\text{O}}] + x. \quad (\text{A.4})$$

For a given deviation from stoichiometry, the concentrations of the point defects can be deduced from the above equations. Experimentally, oxygen defects are dominant for all stoichiometries. This is reproduced by the point defect model provided that  $E_{\text{S}}^{\text{F}}/3 \gg E_{\text{FP}_0}^{\text{F}}/2$ . In this case, three limiting regimes can be distinguished.

Perfect stoichiometry:  $x = 0$  (intrinsic regime)

$$[I_{\text{O}}] = 2[V_{\text{O}}] = \sqrt{2} \exp\left(-\frac{\beta}{2} E_{\text{FP}_0}^{\text{F}}\right), \quad (\text{A.5})$$

$$[V_{\text{U}}] = 2 \exp\left(-\beta\left(E_{\text{S}}^{\text{F}} - E_{\text{FP}_0}^{\text{F}}\right)\right). \quad (\text{A.6})$$

Under-stoichiometry:  $x < 0$

$$[V_{\text{O}}] = -\frac{x}{2}, \quad (\text{A.7})$$

$$[V_{\text{U}}] = \frac{4}{x^2} \exp\left(-\beta E_{\text{S}}^{\text{F}}\right). \quad (\text{A.8})$$

Over-stoichiometry:  $x > 0$

$$[I_{\text{O}}] = x, \quad (\text{A.9})$$

$$[V_{\text{O}}] = \frac{1}{x} \exp\left(-\beta E_{\text{FP}_0}^{\text{F}}\right), \quad (\text{A.10})$$

$$[V_{\text{U}}] = x^2 \exp\left(-\beta\left(E_{\text{S}}^{\text{F}} - 2E_{\text{FP}_0}^{\text{F}}\right)\right). \quad (\text{A.11})$$

The apparent formation energies of the vacancies sites are then defined by

$$E_{V_{\text{X}}}^{\text{F,app}} = -kT \ln([V_{\text{X}}]). \quad (\text{A.12})$$

This expression lead to the values of Table 3.

Plane wave results of Ref. [16] are in quite good agreement with experimental estimates of the formation energies of point defects. However a problem arises when they are analysed in the point defect model for the over-stoichiometric regime (see Ref. [16] for a thorough discussion of this point). The condition  $E_{\text{S}}^{\text{F}}/3 \gg E_{\text{FP}_0}^{\text{F}}/2$  is not verified for the relaxed plane wave results which consequently lead to the accommodation of over-stoichiometry with uranium vacancy. This discrepancy may be due to weaknesses of the energetic model (i.e. weakness of the LDA calculations) or to the neglect of point defect assemblies, especially the so-called Willis clusters of oxygen interstitials [29] that may possibly be important for the accommodation of over-stoichiometry in urania. However this problem does not arise for unrelaxed values on which the discussion are based in the present paper.

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