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# Molecular modelling of transmutation fuels and targets

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## Abstract

The stability of point defects and the behaviour of rare gases in uranium dioxide have been studied using electronic structure calculations. Krypton atoms are found to be insoluble in $UO_2$ whatever the trapping site considered. Their presence induces a swelling of the lattice when they are located in interstitial sites or in oxygen vacancy sites. Due to its smaller atomic size, the predicted helium behaviour is very different. Indeed, helium is found to be soluble in stoichiometric and hyperstoichiometric uranium dioxide in the presence of uranium vacancies or divacancies. Moreover helium atoms induce a lattice contraction except in interstitial sites for which a slight expansion is found. Some preliminary results concerning xenon are also given.
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In the intervening time between the acceptance of the paper and its publication, the department has been struck by the tragic loss of Thierry Petit at the age of 33. He was at the head of the LLCC, the laboratory which he had founded four years ago, and was unanimously recognised by his friends and colleagues as a brilliant scientist whose competence, knowledge and enthusiasm were inspiring. Thierry was a very kind hearted person, perpetually attentive to his colleagues' personal situations. He was also a husband and father of two young children and his friends and colleagues wish to extend their deepest sympathy to his grieving family. Thierry will be sorely missed by all who knew him.

## 1. Introduction

Krypton and xenon are produced in nuclear fuels by fission. It is well established that, depending on burn up and temperature conditions, these two rare gases precipitate to create intra and intergranular bubbles in uranium dioxide. Inert gases also diffuse to free surfaces where they are released to the fuel rod free volumes. So, during reactor operation, the behaviour of xenon and krypton has a direct influence on fuel swelling and more generally on the mechanical behaviour of the rod.

Helium is created by α-decay of heavy elements such as minor actinides and for a negligible part by ternary fission. This rare gas is also used as fill gas for the fuel rod. We can note that, unlike fission gas products, the production of helium continues well after assembly discharge. In the case of mixed oxide (MOX) fuel this production is even much larger after fuel download than during operation. As a consequence, in the case of a transmutation fuel enriched with elements such as neptunium, americium and/or curium, helium release is liable to impact rod pressure.

After a brief presentation of the calculation method, the results obtained for incorporation and solution energies of helium, krypton and xenon in uranium dioxide are discussed and compared to previous studies using the Mott–Littleton simulation technique [1–4]. The

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swelling due to the insertion of fission products in a nuclear fuel oxide is also evaluated. In the case of helium, it is compared to the lattice parameter evolution due to α-irradiation damage.

This theoretical approach is coupled with an experimental programme essentially based on X-ray absorption spectroscopy, which will help to confirm on an atomic scale the relevance of the theoretical data. Some preliminary results of this programme are presented in another article of this issue [5].

## 2. Calculation details

The technique used is based on the local density approximation (LDA) applied to the density functional theory (DFT). The calculations have been performed in the framework of the linear muffin-tin orbital (LMTO) method in the atomic sphere approximation (ASA). This method is detailed elsewhere [6,7]. It has been applied recently to the case of uranium dioxide in order to study point defects and fission product stability [8–13].

The calculations are performed with periodic boundary conditions. This implies that the elementary cell is reproduced to infinity. A supercell has therefore to be taken as large as possible in order to minimize the interaction between two consecutive defects. The calculation time constraint makes it possible to study a maximum size supercell made up of 24 atoms and eight empty spheres (Fig. 1). Empty spheres are added in all the unoccupied octahedral sites of the fluorite structure (space group $Fm\bar{3}m$) of uranium dioxide. This procedure improves the accuracy of the description of the electron charge density by diminishing the overlap between the atomic spheres. Due to the ASA approximation, lattice relaxation cannot be modelled. The atom coordinates are always those of the perfect lattice. However, in each case, the minimum energy is determined as a function of the cell volume, so that the swelling of uranium dioxide
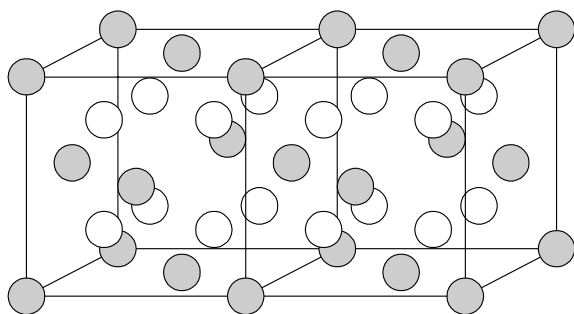


Fig. 1. Perfect supercell of uranium dioxide. The white and grey spheres represent oxygen and uranium atoms respectively. For the sake of clarity, empty spheres occupying all the octahedral sites are not reproduced.

in the presence of point defects or fission products can be estimated for all the configurations studied (See Ref. [10] for details).

The orbital base comprises 7s, 6p, 6d and 5f orbitals for uranium; 2s, 2p, 3d and 4f for oxygen; 1s, 2p, 3d and 4f for helium; 4s, 4p, 4d and 4f for krypton; and 5s, 5p, 5d and 4f for xenon. For calculations involving krypton, the conditions imposed on the atomic sphere radii are $R_{Kr} = 1.05 \ R_U = 1.155 \ R_O = 1.155 \ R_{ES}$ where $R_{Kr}$, $R_U$, $R_O$ and $R_{ES}$ are the krypton, uranium, oxygen and empty sphere radii respectively. In the case of helium, the radii are set according to the following equations: $R_U = 1.25$ $R_{He} = 1.1 \ R_O = 1.1 \ R_{ES}$ where $R_{He}$ is the helium radius. Finally, for xenon, these conditions are $R_{Xe} = 1.1$ $R_U = 1.21 \ R_O = 1.21 \ R_{ES}$ where $R_{Xe}$ is the xenon radius. All summations over the irreducible part of the Brillouin zone involve 63 k points.

## 3. Results and discussion

### 3.1. Incorporation energies

In order to study the stability of helium, krypton and xenon atoms in uranium dioxide, incorporation energies for each element in each trapping site considered are calculated. The results are given in Table 1 and compared to previous studies [1–4] which used a semi-empirical simulation technique. The definition of incorporation energy provided by Grimes et al. [1,2,14] is given by the following Eq. (1):

Incorporation energy

= Fission product substitution energy

− Energy of empty trap site.　　(1)

This definition supposes that there are always much more available trap sites than rare gas atoms. It should then only be used when fission product concentrations are very small i.e. at very low burn up. However, during irradiation or intermediate storage at low temperature, nuclear fuels are not at equilibrium from a thermodynamic point of view. If they were it would be possible to detect stable fission product compounds such as caesium iodide or oxide precipitates [15] in irradiated pressurized water reactor fuels. The radiation environment produces point defects on the oxygen and uranium sub-lattices far in excess of thermodynamic equilibrium values. It is therefore relevant to assume the existence of these defects and to calculate incorporation energies as a function of the trapping site considered.

All incorporation energies calculated for krypton in the present work are positive. This means that some energy has to be provided to incorporate this element in uranium dioxide. The minimum incorporation energy is found for a neutral trivacancy. This is a consequence of

Table 1
Calculated incorporation energies ($E_{in}$) for helium, krypton and xenon atoms in uranium dioxide

| Fission atom position | He | | Kr | | Xe | |
|---|---|---|---|---|---|---|
| | $E_{in}$ (eV) (this work) | $E_{in}$ (eV) (Ref. [2]) | $E_{in}$ (eV) (this work) | $E_{in}$ (eV) (Ref. [2]) | $E_{in}$ (eV) (this work) | $E_{in}$ (eV) (Ref. [2]) |
| Interstitial | 1.3 | −0.13 | 14.2 | 13.3 | 19.0 | 17.2 |
| Oxygen vacancy | 2.2 | −0.12 | 8.0 | 9.9 | Not calculated | 13.3 |
| Uranium vacancy | −7.4 | −0.05 | 3.0 | 3.8 | Not calculated | 5.0 |
| Divacancy | −6.6 | −0.09 | 2.4 | 2.4 | Not calculated | 2.8 |
| Neutral trivacancy | $-6.0 < E_{in} < -5.9$ | −0.08 | $1.4 < E_{in} < 2.2$ | 1.1 | Not calculated | 1.2 |

the chemical inertness and of the size of krypton atoms. Indeed, the Schottky trio defect comprising one uranium vacancy and two oxygen vacancies is the largest trapping site considered in this study. It is noteworthy that present results for krypton are similar to previous results obtained using a quite distinct theoretical approach [2].

The only available value presented in this work for xenon is in good agreement with previous results [2]. At first sight, xenon seems to have a similar behaviour to that of krypton but slight differences could appear due to their different atomic sizes. Additional calculations are in progress.

On the other hand, there are considerable differences in the case of helium. Indeed, the calculations performed by Grimes et al. [2,3] would imply that the site at which helium is incorporated does not play an important role on the equilibrium of the system contrary to predictions for krypton and xenon. Moreover helium incorporation energies calculated in these previous studies are always slightly negative and practically identical. In the present study, the incorporation of helium atoms is exothermal only when they are associated with isolated uranium vacancies or with defect clusters containing uranium vacancies. The most stable trap for helium is the uranium vacancy while Grimes [2] predicted the occupancy of interstitial sites to be slightly more probable. It is quite difficult to explain this major disagreement because the simulation techniques used are based on very different theoretical approaches. The differences observed regarding helium are all the more difficult to explain since results for xenon and krypton are comparable. To summarize, for the semi-empirical method, the absence of the local environment effect on the helium behaviour seems to be questionable. For the present approach, the general trend seems to be better but the strongly negative incorporation energies of helium seems physically unrealistic. This last point is certainly due to the ASA approximation which overestimates the point defect formation energies [11–13]. Finally, we can note that unfortunately the atomic localisation of helium is extremely difficult to obtain experimentally. Its intrinsic properties such as its low mass compared to that of uranium preclude the use of standard techniques such as

Rutherford backscattering spectrometry implemented in a channelling mode.

### 3.2. Solution energies

By definition, an incorporation energy is insensitive to fuel stoichiometry and does not take into account any equilibrium between trapping sites. In order to include these parameters in the present study, solution energies were calculated. They correspond to a theoretical thermodynamic equilibrium state of the fuel. Eq. (2) is again derived from the definition given by Grimes et al. [1,2,14]:

$$\text{Solution energy} = \text{Incorporation energy} + \text{Equilibrium trap formation energy.} \tag{2}$$

The results for krypton and helium are summarised in Tables 2 and 3 respectively. Trap site formation energies were not calculated ab initio. The values obtained by Grimes and Catlow [1] were used. Practically, they are added to the ab initio incorporation energies resulting in the hybrid ab initio/pair potential values [14] presented below.

The positive values for krypton lead to the prediction of the insolubility of this element in uranium dioxide whatever the trapping site and the stoichiometry considered. This is in agreement with previous theoretical studies [1,2]. Experimentally, this conclusion is confirmed by the usual observation of fission gas precipitation

Table 2
Calculated solution energies (eV) for krypton in uranium dioxide

| Krypton atom position | $UO_{2-x}$ | $UO_2$ | $UO_{2+x}$ |
|---|---|---|---|
| Interstitial | 14.2 | 14.2 | 14.2 |
| Oxygen vacancy | 8.0 | 11.4 | 14.8 |
| Uranium vacancy | 16.3 | 9.5 | 2.7 |
| Divacancy | 12.5 | 9.1 | 5.7 |
| Neutral trivacancy | 9.8 | 9.8 | 9.8 |

Table 3
Calculated solution energies (eV) for helium in uranium dioxide

| Helium atom position | $UO_{2-x}$ | $UO_2$ | $UO_{2+x}$ |
|---|---|---|---|
| Interstitial | 1.3 | 1.3 | 1.3 |
| Oxygen vacancy | 2.2 | 5.6 | 9.0 |
| Uranium vacancy | 5.9 | −0.9 | −2.9 |
| Divacancy | 3.5 | 0.1 | −3.3 |
| Neutral trivacancy | 2.5 | 2.5 | 2.5 |

Table 4
Calculated variation of the uranium dioxide lattice parameter in the presence of helium, krypton and xenon atoms

| Rare gas atom position | $\Delta a/a_0$ (%) | | |
|---|---|---|---|
| | He | Kr | Xe |
| Interstitial | 0.25 | 2.3 | 3.3 |
| Oxygen vacancy | −0.25 | 1.7 | Not calculated |
| Uranium vacancy | −1.5 | <0.25 | Not calculated |
| Divacancy | −1.3 | <0.25 | Not calculated |
| Neutral trivacancy | −1.3 | <0.25 | Not calculated |

in intragranular and/or intergranular bubbles. The driving force for krypton release has its origin in this insolubility. For stoichiometric and hyperstoichiometric uranium dioxide that are of interest in the nuclear industry, the most favourable trap sites are the divacancy (association of one uranium and one oxygen vacancy) and the uranium vacancy respectively. No experimental data are available on this subject. The only studies available concern radon [16,17]. Assuming a similar behaviour for all inert gases, Matzke [17] expects xenon to be trapped in defect clusters such as neutral trivacancies in stoichiometric uranium dioxide. Our prediction of divacancies being more favourable for krypton is therefore in fairly good agreement with the experimental evidence available. The fact that krypton is more likely to be associated with divacancies rather than trivacancies is possibly a consequence of its smaller atomic volume. This conclusion has to be moderated by the fact that results for uranium vacancies, divacancies and neutral trivacancies are very close in the case of stoichiometric uranium dioxide.

The results for helium are quite different from those obtained for krypton. First, at equilibrium, helium is soluble in stoichiometric and hyperstoichiometric uranium dioxide. Two different trapping sites are energetically favourable: the uranium vacancy in stoichiometric and hyperstoichiometric uranium dioxide, and the divacancy in hyperstoichiometric uranium dioxide. The helium atomic volume, which is lower than that of krypton, could explain this different predicted behaviour.

Considering the three rare gases of interest in nuclear fuels, it could be concluded that the larger the atom, the larger the favourable trapping site.

### 3.3. Swelling

All the results presented above have been obtained after simulating supercell volume relaxation. The lattice parameter evolution due to the presence of fission gases can then be evaluated as a function of the occupied trapping site. Results are reported in Table 4.

From the results presented in the previous section, at equilibrium, helium atoms would occupy uranium vacancies in stoichiometric uranium dioxide and divacancies in hyperstoichiometric uranium dioxide. In the presence of high concentrations of point defects, helium atoms would occupy uranium vacancies. All these configurations lead to a calculated contraction of the lattice. At first sight, this result could appear to be surprising. Indeed, it is known that the uranium dioxide lattice parameter increases under α-irradiation [18,19]. However Weber attributes this swelling to residual point defects created by irradiation damage rather than to the presence of helium. Current calculations are consistent with this interpretation.

The most stable traps for krypton atoms are calculated to be divacancies in stoichiometric uranium dioxide, uranium vacancies in hyperstoichiometric uranium dioxide and neutral trivacancies in the presence of high point defect concentrations. It appears from Table 4 that the calculated variation in lattice parameter for these three most probable sites is expected to be negligible.

## 4. Conclusion

The present electronic structure calculations suggest that, when point defect concentrations are much higher than rare gas concentrations, uranium vacancies and neutral trivacancies provide the most stable trapping sites for helium and krypton atoms respectively. At equilibrium, the hybrid ab initio/pair potential values obtained lead to a different conclusion. Indeed, in stoichiometric uranium dioxide, results predict the occupancy of uranium vacancies and divacancies for helium and krypton respectively. The insolubility of krypton in uranium dioxide is confirmed. On the other hand helium should be soluble in stoichiometric and hyperstoichiometric uranium dioxide in the presence of divacancies and uranium vacancies. The results would also indicate that krypton and helium atoms, so long as they remain isolated in the matrix, do not contribute to any great extent to the in pile swelling of oxide fuels. Swelling on the other hand could be due to the presence of irradiation-induced point defects, isolated xenon atoms or clusters of fission gas atoms. Calculations concerning xenon in uranium dioxide are in progress and we plan to extend our study to plutonium and americium dioxides in the near future.

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