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Location of krypton atoms in uranium dioxide

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Abstract

For the first time, an ab initio calculation method is applied to study the behaviour of a fission product in uranium dioxide. Among the various considered point defects (interstitial, uranium or oxygen vacancy, divacancy and neutral trivacancy also called Schottky trio defect), the krypton atoms are found to be located preferentially in Schottky trio defects. This result confirms previous theoretical and experimental studies. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

Xenon and krypton are fission products produced with a significant fission yield (more than 25%) in nuclear fuel. So, the behaviour of these noble gases in uranium dioxide must be well understood as it has a large influence on the fuel swelling as well as on the fission gas release. These two later mechanisms could become a limiting factor for reactor operation.

In this paper, the behaviour of single atoms of krypton in uranium dioxide is chosen as a model. Since it is well known that noble gases have a very similar chemical behaviour [1] due to their common closed shell electronic structure but different atomic sizes, one can expect that a study on xenon would lead to similar results if the size effect is not prevalent.

The calculation method is presented in Section 2. It is based on the density functional theory (DFT) in the framework of the local density approximation (LDA). The calculations do not need any adjustable parameter and the method used here is different from the semi-empirical approach currently used by several authors [2–13]. Moreover, in the present LDA approach, the partly covalent character of uranium dioxide is considered whereas molecular dynamics calculations are based on a purely ionic description of this material. The crude approximation made in semi-empirical schemes can explain some discrepancies with the results obtained in the present study. Section 3 is dedicated to the comparison between the results obtained in this study and the theoretical [4,7,9] or experimental [14,15] previous ones. Then the conclusion emphasises the fact that the data obtained using this approach could be very useful to the understanding of the nuclear fuel behaviour and then to its mechanistic modelling.

2. Calculation details

The technique used is based on the LDA applied to the DFT. The calculations have been performed in the framework of the linear muffin-tin orbital (LMTO) method in the atomic sphere approximation (ASA) [16]. This method is detailed in Refs. [17,18].

The LDA approximation leads to a metallic ground state for UO_2 compound [19–21]. In order to improve this result a correction including an on-site Coulomb interaction has to be added [20,21]: this leads to the

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so-called LSDA + U method where the term U describes the correlations between the electrons. However, if LDA fails to reproduce the insulating ground state, the calculations based on this approximation reproduce very well the cohesive properties of UO_2 [19] as well as the experimental trends observed on point defects [22]. Therefore, we think that this approximation is well adapted to the present study and all the results presented in this work have been obtained within this framework.

As in previous papers [19,22], we took advantage of the supercell method. As the calculations are performed in periodic boundary conditions, this implies that the elementary cell containing or not a point defect is reproduced all over the space. Then the supercell has to be taken as large as possible in order to minimise the interaction between a defect and its image. Let us note that this method does not permit one to study the influence of the defect concentration on the results.

Uranium dioxide crystallises in the fluorite structure (space group Fm3m). There are two ways which allow one to describe the crystallography of this compound. The first one is a face centred cubic array of uranium cations in which all the tetrahedral sites are occupied by oxygen anions. The second one is a primitive cubic array of anions with one half the cube centres occupied by cations. Let us mention that the two descriptions give identical results for total energy calculations. We will particularly use the first definition in the following.

In order to minimise the interaction between two point defects, a supercell constituted by 24 atoms and eight empty spheres was used (Fig. 1). Empty spheres are added in all the unoccupied octahedral sites of the fluorite structure. They permit one to improve the accuracy of the description of the electron charge density by diminishing the overlap between the atomic spheres.

The coordinates of the atoms are always those of the perfect lattice. However, in each case, the minimum energy is determined as a function of the cell volume. So, we can have an information about the swelling of the nuclear fuel in the presence of krypton atoms.

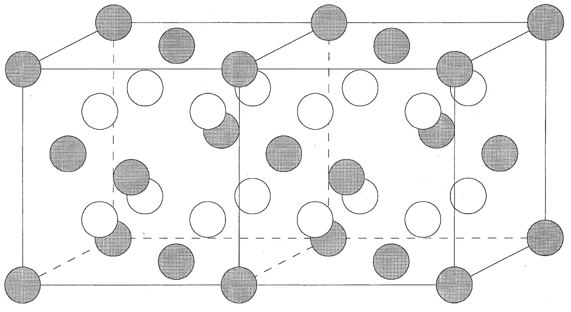

Fig. 1. Perfect supercell of uranium dioxide (U_8O_{16}). The white and grey spheres represent oxygen and uranium atoms, respectively. For the sake of clarity, empty spheres occupying all the octahedral sites are not reproduced.

The basis set contained 7s, 6p, 6d and 5f orbitals for uranium, 2s, 2p, 3d and 4f for oxygen and 4s, 4p, 4d and 4f for krypton (see [19] and references therein for more details). 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. All the summations over the irreducible part of the Brillouin zone involve 63 k points.

3. Results and discussion

When a krypton atom is created by fission, a lot of crystallographic sites can be considered for its location in the uranium dioxide matrix. Among them, we chose to study the interstitial position, the uranium and oxygen vacancies, the divacancy constituted by one uranium and one oxygen vacancy, and the neutral trivacancy also called Schottky trio defect. This last point defect consists of one uranium and two oxygen vacancies. It can adopt three different geometrical configurations (Fig. 2).

The results are summarised in Table 1. For the sake of clarity and homogeneity, we used the definition of the solution energy provided by Grimes et al. [7,9]. Thus, for the case of krypton substituted at a pre-existing uranium vacancy site, the solution energy, E_s, is given by

$$\begin{aligned}&\text{solution energy}\\&\quad= \text{energy of lattice containing a gas atom}\\&\qquad- \text{energy of lattice with uranium vacancy}\\&\qquad- \text{self-energy of krypton.}\end{aligned}$$

We have also applied this definition to the data given by Catlow [4]. So the results presented here can be directly compared to the previous ones published in the literature. The different solution energies determined in this study for the presence of a krypton atom in a trivacancy depend on the three possible geometrical configurations of this point defect. The most stable configuration, i.e., $E_s = 1.4$ eV, is the one constituted by a uranium vacancy and the two oxygen vacancies situated on the edge of an oxygen cube (Fig. 2(e)). When the two oxygen vacancies form a diagonal of an oxygen cube face (Fig. 2(g)), the calculations give a solution energy of 1.9 eV. Lastly, when a krypton atom is included in a linear trivacancy (Fig. 2(f)), we find a solution energy of 2.2 eV. The differences in the literature are related to the successive improvements of the potentials used to make the calculations. At first sight the agreement between all the numerical results is good.

The positive values clearly show that in all the cases studied some energy has to be given to the system in

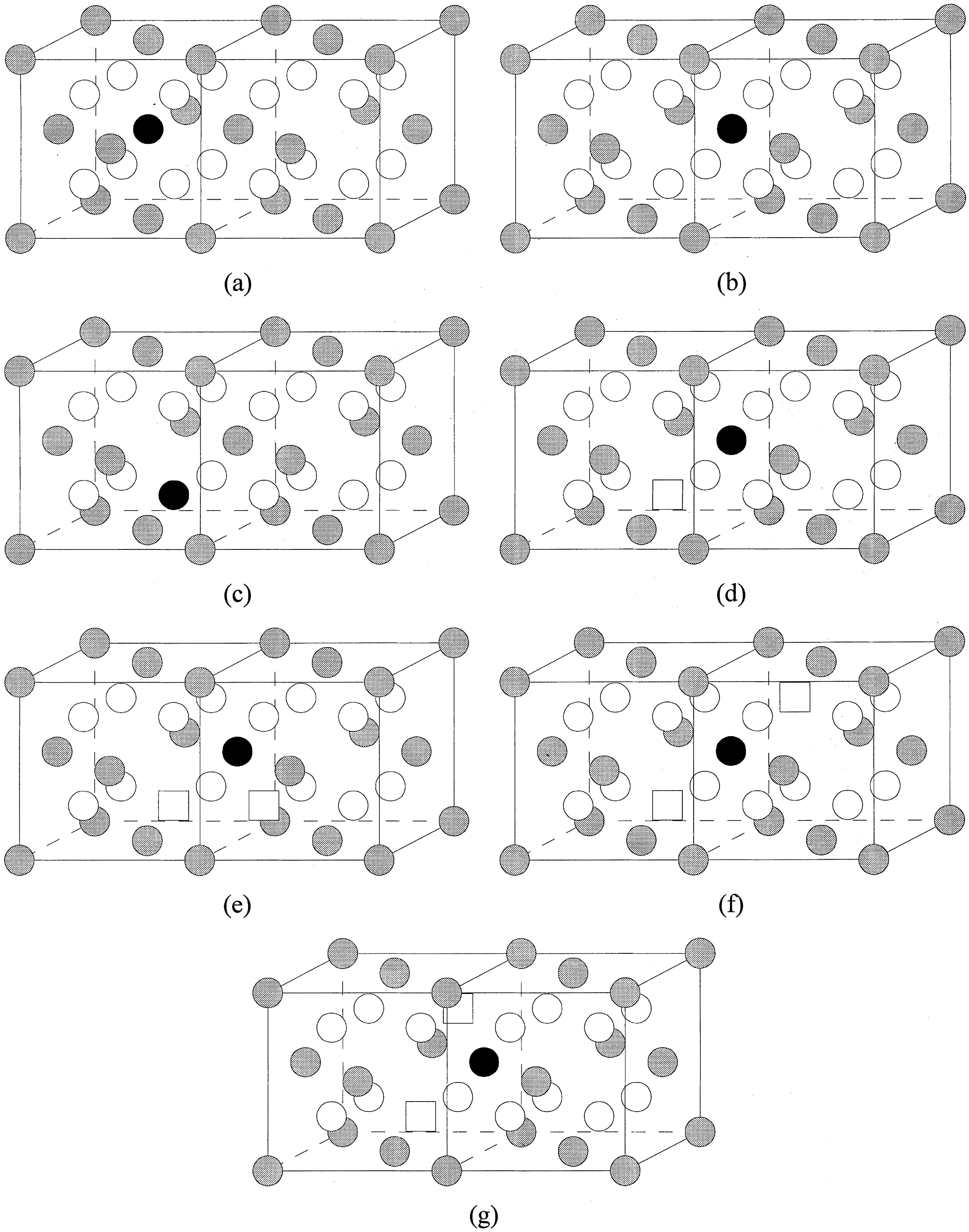

Fig. 2. Supercells used during the calculations of solution energy. The white, black and grey spheres represent oxygen, krypton and uranium atoms, respectively. The white squares represent oxygen vacancies. The krypton atom is respectively in: (a) an interstitial position, (b) substitution of a uranium atom, (c), substitution of an oxygen atom, (d) a divacancy (in the uranium vacancy position), (e), (f) and (g) a trivacancy (in the uranium vacancy position).

Table 1
Calculated solution energies (E_s) of a krypton atom in uranium dioxide

Krypton atom position	Solution energy (eV) (this work)	Solution energy (eV) (literature)
Interstitial	14.2	8.1 [4] $< E_s <$ 13.3 [9]
Oxygen vacancy	8.0	6.4 [4] $< E_s <$ 9.9 [9]
Uranium vacancy	3.0	1.5 [4] $< E_s <$ 6.0 [7]
Divacancy	2.4	5.7 [9]
Neutral trivacancy	$1.4 < E_s < 2.2$	0.7 [4] $< E_s <$ 9.5 [9]

order to insert a krypton atom in the fuel lattice. So it is confirmed that krypton is not soluble in uranium dioxide, at least to such high concentration (4 at.%).

In the present work, the minimum in the solution energy is clearly obtained when a krypton atom occupies a neutral trivacancy. So we predict that at equilibrium this fission product is present in Schottky defects. This result is in agreement with experiments [14,15] based on Rutherford backscattering spectroscopy which show that a rare gas atom is not located in uranium nor oxygen single vacancies and do not occupy the large interstitial site in UO_2.

Previous theoretical studies [4,9] include the effect of stoichiometry on the lattice site adopted by fission products. In this way, these authors respectively suggest that in UO_{2-x} the oxygen vacancy [4] and the trivacancy [9] provide the lowest solution energy for krypton. In stoichiometric uranium dioxide, they predict that solution of krypton can occur at cation vacancy [4] or at a divacancy site [9]. At last, in UO_{2+x} they agree about the trapping of krypton atoms in uranium vacancies. In the present study, due to the computation method itself and then to the size of the supercell used, it is not possible to evaluate the influence of the stoichiometry on krypton trapping. However, present calculations on interstitials and neutral trivacancies are made with a stoichiometric supercell. So an important discrepancy (factor greater than four) is observed between the present results and the value obtained by Grimes et al. [9] for the insertion of a krypton atom in a Schottky defect. This discrepancy is quite puzzling since the agreement with these authors is correct for simple point defects (interstitial, oxygen and uranium vacancies) but very poor for more complex structures (divacancy and neutral trivacancy). The results on oxygen vacancies have to be compared to the hypostoichiometric data found in the literature. In the same manner, the results on divacancies and uranium vacancies are obtained with hyperstoichiometric supercells. In this last case, contrary to other theoretical studies but in better agreement with experiment [14,15], the present calculations show that krypton is slightly more stable in divacancies than in uranium vacancies.

Another interesting feature is the evolution of the fuel lattice parameter in presence of a krypton atom. Table 2 suggests a slight expansion only when krypton is trapped in interstitial positions or oxygen vacancies. It is worth emphasising the crystallography of the different sites. If we consider the interstitial position and the oxygen and uranium substitutions, we can see that only the Kr–U distances are very different. Indeed, if a krypton atom occupies an interstitial, i.e., an octahedral empty site, it has eight oxygen nearest neighbours situated at 2.37 Å and six uranium atoms at 2.74 Å. In an oxygen vacancy, the krypton atom is surrounded by four uranium atoms at 2.37 Å and by six oxygen atoms at 2.74 Å. Lastly, in a uranium vacancy, the nearest neighbours of the krypton atom are eight oxygen atoms at 2.37 Å and twelve uranium atoms at 3.87 Å. Considering these data and the results presented in Table 2, we can see that there is no increase of the lattice parameter of UO_2 in presence of a krypton atom if the Kr–U distance is superior to 2.74 Å. So the fuel swelling due to this fission product should be quite small at equilibrium since we predict that krypton occupies neutral trivacancies.

Table 2
Calculated lattice parameter variation of uranium dioxide as a function of the site occupied by a krypton atom

Krypton atom position	Lattice parameter variation (%)
Interstitial	+2.3
Oxygen vacancy	+1.7
Uranium vacancy	<0.25
Divacancy	<0.25
Neutral trivacancy	<0.25

4. Conclusion

The present electronic structure calculations suggest that the trivacancy trap in its most compact geometrical configuration provides the lowest solution energy for krypton in uranium dioxide. This result is in agreement with experiment but in contradiction with previous theoretical studies [9]. The very low solubility of krypton in nuclear fuel is confirmed. The swelling due to the presence of krypton atoms in the fuel lattice should be negligible since it is apparent only for non stable traps.

We plan to study other fission products in a near future and to extend the calculations to the MOX fuel.

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