Journal of Nuclear Materials 385 (2009) 368–371

Contents lists available at ScienceDirect

Journal of Nuclear Materials

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

Ab initio study of solution energy and diffusion of caesium in uranium dioxide

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ARTICLE INFO

PACS:
71.15.Mb
71.27.+a
61.80.Az
61.82.Ms

ABSTRACT

The behaviour of caesium in nuclear fuels is investigated using density functional theory (DFT). In a first step, the incorporation and solution energies of Cs in pre-existing trap sites of UO_2 (vacancies, interstitials, U–O di-vacancy and Schottky trio defects) are calculated using the projector-augmented-wave (PAW) derived pseudopotentials as implemented in the Vienna ab initio simulation package (VASP). Correlation effects are taken into account within the DFT + *U* approach. The solubility of caesium is found to be very low, in agreement with experimental data. The migration of Cs is found to be highly anisotropic, it is controlled by uranium diffusion with an Arrhenius activation energy of 4.8 eV in hyperstoichiometric UO_{2+x}, in good agreement with experimental values.

1. Introduction

Caesium is an important fission product produced in relatively large quantities in a nuclear reactor during the irradiation of the UO_2 fuel. Due to its quite significant fission yield ($\sim$0.197 for its stable and long life isotopes) and the associated high radiotoxicity, principally due to the γ activity of its isotope 137, caesium is very important in studies related to nuclear safety. In the case of a hypothetical severe nuclear accident leading to reactor core fusion, this element can be released in large quantities in the reactor containment building, and some amount may subsequently reach the outside environment through containment leakages. Therefore, a basic understanding of the mechanisms controlling its release behaviour to the environment is of crucial importance. In this context, one of the aim of the 'Institut de Radioprotection et de Sûreté Nucléaire' (IRSN) is the understanding of fission products behaviour in uranium dioxide.

The distribution of the fission products in the fuel is controlled by a number of parameters, such as the solubility in the fuel, the mobility, the chemical affinity with other products for elements that are reactive. Their subsequent behaviour greatly depends on the temperature and the oxygen potential of the fuel. The solubility of caesium is low in the fuel (0.07 mass% in UO_2 at 2173 K) [1]. A large fraction of this fission product migrates within the fuel grains and accumulates at the grain boundaries where it can contribute to the growth of fission gas bubbles. It can be released from the fuel due to the interconnection of fission gas bubbles or interact with oxygen to form oxides, or with iodine to form CsI, or participate in the formation of several solid phases by interacting with the fuel, the transition element fission products and the clad [2–4].

The enthalpies of solution and migration are very important parameters in the mechanistic models of a fission product release since the first step in its release is its migration to the grain boundaries. Therefore, this paper is focused on the theoretical determination of solution and migration energies of caesium in uranium dioxide. Previous theoretical calculations for caesium solubility [5] and migration [6] were based on semi-empirical interatomic potentials with limited reliability. Density functional theory (DFT) calculations have also been performed previously on the solubility of caesium in UO_2 on small unit cells neglecting atomic relaxation effects which may alter their reliability [7]. Moreover, these calculations used the local density approximation that is known to give a qualitatively incorrect description of the strongly correlated 5f-electrons of uranium. In a recent contribution [8], the GGA + *U* functional was used, it is known to improve the description of the electronic structure of UO_2 since it takes into account the effects due to the localization of the f-electrons of uranium in this compound. Our results on formation energies of point-defects show that this f-electron localization modifies formation energies of uranium point-defects more strongly than those of oxygen. Then it is suspected that the f-electron localization may have also profound implications upon fission product behaviour. In this contribution, such calculations are extended to the solution and migration energies of Cs in UO_2 in order to check the sensitivity of ab initio based results to the choice of exchange-correlation functionals. Such results must also provide a better understanding in the release characteristics of Cs. Since the solution energy depends on the stoichiometry, it was also determined for the sub-stoichiometric UO_{2-x}, as well as for over-stoichiometric UO_{2+x}. Several sites for the incorporation of Cs have been considered in

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doi:10.1016/j.jnucmat.2008.12.009

the present work, and include U vacancy, O vacancy, interstitial site, U–O di-vacancy complex, and the Schottky defects. The solubility of Cs is found to be extremely low in UO_2 in all cases which is in agreement with the experimental data of Walker et al. [9] and Kleykamp [1]. Migration of Cs was shown to be highly anisotropic, and controlled by uranium diffusion with an Arrhenius activation energy of 4.8 eV in hyperstoichiometric UO_{2+x}, in good agreement with experimental values. In what follows a brief description of the computational details, a discussion of our results, and concluding remarks are provided.

2. Methodology

Density functional (DFT) calculations of total energy were performed with the projector-augmented-wave (PAW) method [10] as implemented in the Vienna ab initio Simulation Package (VASP) [11,12]. All the calculations are performed within DFT with the generalized gradient approximation (GGA) and the GGA + U approximation that takes into account the electronic correlations present in UO_2 since GGA + U is found to be superior to LDA + U to describe cohesive properties of materials with strong electronic correlations [13]. The Hubbard U correction is introduced to describe strongly correlated uranium 5f-electrons. The rotationally invariant form of GGA + U is used with a spherically averaged double counting term [14]. Within this approximation, there is a single parameter $U_{\mathrm{eff}} = U–J$, where U is the averaged Hubbard parameter and J represents the screened exchange energy. U_{eff} is chosen to be equal to 4 eV for all the studied compounds. Such a value is also very close to the value used by Dudarev et al. [15] or by Laskowski et al. [16] and to the experimental findings [17,18].

A plane-wave basis set with a cutoff energy of 480 eV was used in all calculations. Brillouin zone sampling using a $4 \times 4 \times 4$ k-point grid was found necessary for differences of total energies and magnetic moments of our $2 \times 2 \times 2$ primitive cell of UO_2 (96 atoms) to converge within 10^{-3} eV and 0.01 μ_B, respectively. Structural optimizations were carried out at constant volume and under the condition that all residual forces should be smaller than 0.01 eV $Å^{-1}$. Within GGA, the volume is fixed using equilibrium lattice constant to 5.38 Å while the lattice constant is equal to 5.52 Å in GGA + U [8]. In this latter case, let us mention that the antiferromagnetic structure in accordance with experimental results was assumed [19,20]. The spin-orbit has been neglected since it has been shown that it affects only the long range magnetic ordering that has minor effects on cohesive properties of UO_2 [16]. Finally, even if entropy calculations should be considered to study fission products solution in uranium dioxide, they were neglected hereafter.

3. Discussion

3.1. Incorporation energies

The incorporation energy, E^{inc}, of caesium atom in uranium dioxide defects and in the octahedral interstitial site have been calculated using the supercell containing 96 atoms. The crystallographic defects taken into account are the oxygen and uranium vacancies, oxygen–uranium di-vacancy and Schottky or neutral tri-vacancy [8]. The incorporation energy is obtained from the calculated energies of supercells with and without Cs atom:

$$E^{\mathrm{inc}}_{\mathrm{Cs}\in X} = E_{\mathrm{Cs}\in X} - E_X - E^{\infty}_{\mathrm{Cs}}, \tag{1}$$

where $E_{\mathrm{Cs}\in X}$ is the energy of the supercell containing Cs in site X. E_X is the energy of the supercell containing a defect site of type X, E^{∞}_{Cs} is the energy of the isolated Cs atom. The incorporation energies using GGA and GGA + U functionals are reported in Table 1 and compared with previous results [5,7]. In all cases, the most stable sites are shown in bold characters. In GGA, the lowest incorporation energy corresponds to the Schottky defect, followed by the di-vacancy and the uranium vacancy. In GGA + U, the hierarchy between these three sites is different, the uranium vacancy giving the most negative incorporation energy. Let us mention that our GGA + U results are in qualitative agreement with the semi-empirical results of Grimes and Catlow [5] but differ strongly from previous ab initio calculations. However, too small unit cells used in these previous ab initio calculations limits their reliability [7]. The incorporation energies may be understood on the basis of a competition between size effects due to the incorporation of Cs and bond formation of Cs with the neighbouring oxygen atoms. From our results, it can be concluded that GGA + U as opposed to GGA favours the bond formation or chemical interactions since the uranium vacancy that displays the greatest number of oxygen atoms as first nearest neighbours is the most favourable site.

Table 1
Incorporation energies of caesium in uranium dioxide. Int is an interstitial octahedral site of the lattice, v_O and v_U are, respectively, an oxygen and an uranium vacancy, $2v$ is a U–O di-vacancy complex, and Sch is a Schottky defect. Note that the values in bold characters correspond to the most stable sites for the incorporation of caesium.

Site	GGA	GGA + U	Ref. [7]	Ref. [5]
E^{inc} (eV)				
Int	10.24	7.53	15.0	9.93
v_O	8.24	6.41	17.9	9.10
v_U	0.90	**−1.20**	3.6	**−6.08**
$2v$	**0.38**	−1.12	–	−5.62
Sch	**0.32**	−0.61	–	−5.47

3.2. Solution energies

The use of the incorporation energies is limited since it is not sensitive to the concentrations of the different insertion sites. To take into account this concentration dependence, the solution energy should be considered. In fact, the solution energy $E^{\mathrm{sol}}_{\mathrm{Cs}\in X}$ takes into account the formation energy of the defect X at equilibrium as

$$E^{\mathrm{sol}}_{\mathrm{Cs}\in X} = E^{\mathrm{inc}}_{\mathrm{Cs}\in X} + E^{\mathrm{Fapp}}_X, \tag{2}$$

where E^{Fapp}_X is the apparent formation energy of defect X, which depends on temperature and on the deviation from stoichiometry through the following expression:

$$E^{\mathrm{Fapp}}_X = -k_B T \ln([X]). \tag{3}$$

Apparent formation energies can be expressed in the framework of the point-defect model introduced by Matzke [21] and Lidiard [22] to obtain the concentration of defects in UO_2 and their dependence with stoichiometry. As a first estimation, defect concentrations can be estimated by considering that they are dominated by oxygen vacancies (respectively oxygen Frenkel pairs and oxygen interstitials) in UO_{2-x} (respectively UO_2 and UO_{2+x}). Using this simplified model as proposed by these authors, one can get the expressions of E^{Fapp} reported in Table 2. They depend on energies of the oxygen Frenkel pairs, E_{PFo}, and Schottky defect, E_S while B_{2v} and B_S are the binding energies of di- and tri-vacancies. These values are reported in Table 3 for GGA and GGA + U functionals. The estimated values of solution energies from our calculations at $T = 0$ K are then given in Table 4. One can observe that caesium is preferentially inserted in a uranium vacancy for UO_{2+x} using both functionals. In UO_2, the preferential site is still the uranium vacancy in GGA and the di-vacancy in GGA + U. In UO_{2-x}, the preferential site is the Schottky defect for both functionals. However, the general trend is similar in both sets of calculations. The solubility of Cs is found to be very low in agreement with experimental

Table 2
Expressions of apparent formation energies of defects in uranium dioxide. v_O and v_U correspond, respectively, to an oxygen and an uranium vacancy, $2v$ is a di-vacancy and Sch is a Schottky defect. B_S and B_{2v} are, respectively, the binding energies of a Schottky defect and a di-vacancy, and E_{PF_O} is the formation energy of an oxygen Frenkel pair.

X	UO_{2-x}	UO_2	UO_{2+x}
E_X^{Fapp}			
v_O	$-k_BT\ln\left(\frac{\lvert x\rvert}{2}\right)$	$\frac{E_{PF_O}}{2}+\frac{k_BT}{2}\ln(2)$	$E_{PF_O}+k_BT\ln(x)$
v_U	$2k_BT\ln\left(\frac{\lvert x\rvert}{2}\right)+E_S$	$E_S-E_{PF_O}-k_BT\ln(2)$	$E_S-2E_{PF_O}-2k_BT\ln(x)$
$2v$	$E_S-B_{2v}+k_BT\ln\left(\frac{\lvert x\rvert}{2}\right)$	$E_S-\frac{E_{PF_O}}{2}-B_{2v}-\frac{k_BT}{2}\ln(2)$	$E_S-E_{PF_O}-B_{2v}-k_BT\ln(x)$
Sch	E_S-B_S	E_S-B_S	E_S-B_S

Table 3
Values of apparent formation energies (eV) calculated in GGA and GGA + U at T = 0 K. v_O and v_U correspond, respectively, to an oxygen and an uranium vacancy, $2v$ is a di-vacancy and Sch is a Schottky defect.

	E_X^{Fapp} GGA (eV)			E_X^{Fapp} GGA + U (eV)		
	UO_{2-x}	UO_2	UO_{2+x}	UO_{2-x}	UO_2	UO_{2+x}
X						
v_O	0	1.8	3.6	0	2.0	4.0
v_U	5.2	1.6	−2.0	7.2	3.2	−0.8
$2v$	4.7	2.9	1.1	3.3	1.3	−0.7
Sch	4.3	4.3	4.3	1.5	1.5	1.5

Table 4
Solution energies of caesium in uranium dioxide. Int is an interstitial octahedral site of the lattice, v_O and v_U are respectively an oxygen and a uranium vacancy, $2v$ is a U–O di-vacancy complex, and Sch is a Schottky defect. Note that the values in bold characters correspond to the most stable sites for the solution of caesium.

	E^{sol} GGA (eV)			E^{sol} GGA + U (eV)			E^{sol} (eV) Ref. [5]		
	UO_{2-x}	UO_2	UO_{2+x}	UO_{2-x}	UO_2	UO_{2+x}	UO_{2-x}	UO_2	UO_{2+x}
Site									
Int	10.2	10.2	10.2	7.5	7.5	7.5	9.9	9.9	9.9
v_O	8.2	10.0	11.8	6.4	8.4	10.4	9.1	12.5	15.9
v_U	6.1	**2.5**	**−1.1**	6.1	2.0	**−2.0**	7.3	**0.4**	**−6.4**
$2v$	5.1	3.3	1.5	2.2	**0.2**	−1.8	4.5	1.1	−2.4
Sch	**4.6**	4.6	4.6	**0.9**	0.9	0.9	**2.9**	2.9	2.9

features and appears to increase slightly in the over-stoichiometric regime. In Table 4, the solution energies estimated in the framework of Mott–Littleton method [5] are also reported. They are qualitatively in agreement with our results even if the solubility of Cs seems to be overestimated in the over-stoichiometric regime.

3.3. Migration energies

Activated migration mechanisms consist of sequential jumps of the migrating atom between vacant lattice sites or between interstitial sites. The activation energy for the migration process, once the defects are in registry, is the difference between the energy of the system when the migrating atom is at the saddle point and the energy of the atom in the trap site adjacent to the defect that mediates the migration mechanism. Here, the climbing image nudged elastic band (NEB) method is applied to locate the transition state, and typically four slab replicas between the initial and final states are sufficient to produce a smooth minimum energy path [23]. A spline interpolation fit was also used to examine the stability of the NEB calculations and determine the potential energy barriers more accurately. In the previous section, caesium is predicted to be insoluble in UO_{2-x} and UO_2 but becomes slightly soluble in UO_{2+x} as the uranium vacancies necessary to accommodate caesium are more easily formed in UO_{2+x}. Then in UO_{2+x}, Cs atom migration will occur via a uranium vacancy assisted migration mechanism. In such a mechanism, two effects are in competition, either the migration energy of Cs from one uranium vacancy to the next or the self-diffusion of the uranium vacancy. If the self-diffusion process has a higher activation energy than the migration process itself, then the observed Cs migration energy will be that of the self-diffusion process.

Table 5
Arrhenius activation energies, $E_{v_U}^{Arr}$, of uranium vacancies in uranium dioxide.

	GGA	GGA + U	[24]	[21]
$E_{v_U}^{Arr}$ *(eV)*				
UO_{2-x}	11.0	12.8	17.3	~7.8 ($x < 0.02$) ~5 ($x \geqslant 0.02$)
UO_2	7.4	8.8	12.6	5.6
UO_{2+x}	3.8	4.8	7.8	2.6

Firstly, the results for the migration of uranium vacancies are discussed. Calculations were performed along the [1 0 0] and [1 0 1] directions. For GGA, a value of 6.31 eV and 5.80 eV for [1 0 0] and [1 0 1] directions respectively is obtained while GGA + U gives 8.24 and 5.60 eV. It can be concluded that the migration of the uranium vacancy is anisotropic and occurs preferentially in the [1 0 1] direction. In order to take into account the deviations from stoichiometry, the point-defect model [21,22] that attributes the observed changes in metal-atom diffusion coefficients solely to the changes in defect concentrations, can be used. The so-obtained Arrhenius activation energies are reported in Table 5 and compared with either experimental data or previous semi-empirical calculations. Ab initio calculations give a better agreement with experimental results.

Next, the migration energy of caesium is determined. Using GGA + U, they are equal to 4.6 and 2.7 eV along the [1 0 0] and [1 0 1] crystallographic directions respectively. As for migration of uranium, the migration of caesium is anisotropic and occurs preferentially along the [1 0 1] direction. It should be noted, however, that in the [1 0 1] direction, the atomic relaxations around the migrating atom and the migrating atom itself are relatively large for both uranium and caesium diffusion while they are reasonable in the [1 0 0] direction. These energies of migration are clearly lower than the corresponding energies of uranium migration with similar approximations, showing that the activation energy for Cs migration is lower than the uranium activation energy for self-diffusion, which is thus predicted to be the controlling step in the migration mechanism of Cs. Prussin et al. [25] found a migration energy of 4.3 ± 0.5 eV for Cs migration in uranium dioxide and Akabori and Fukuda [26] predict a migration energy of caesium of 4.8 eV in $(U,Th)O_2$ fuel at very low burnup. These values are in good agreement with our calculated value (4.8 eV in GGA + U) of uranium diffusion in hyperstochiometric UO_{2+x}.

4. Conclusion

The solution energy predictions by means of ab initio calculations are consistent with the experimental observations that caesium is insoluble in UO_2 and UO_{2-x}. In the over-stoichiometric regime, caesium is found to be slightly soluble, the preferential trap site being the uranium vacancy. From the study of activation migration mechanisms it can be concluded that the self-diffusion of the uranium vacancy is the controlling step in the migration mechanism. However, it is possible that this later conclusion can be modified in highly irradiated uranium dioxide fuel since it is known that uranium diffusivity can be greatly enhanced by radiation damage. As a reactive element, caesium may be involved in the formation of several solid phases through its interaction with some fission products and also with fuel and clad components

[3,4]. For example, it may interact with oxygen to form oxides, with iodine to form iodide or with transition metal elements such as Mo to form caesium molybdates, Zr to form zirconates, uranium to form uranates, etc. The formation of these phases at the grain boundaries and the release of Cs at a given temperature are intimately dependent on the oxygen potential of the fuel. Their role needs to be fully investigated for a complete understanding of the behaviour of Cs.

Acknowledgement

The authors would like to acknowledge EDF company that contributed to the support of this work.

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