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An atomistic approach to self-diffusion in uranium dioxide

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ABSTRACT

The formation and mobility of point defects in UO_2 have been studied within the framework of the Density Functional Theory. The *ab initio* Projector Augmented Wave method is used to determine the formation and migration energies of defects. The results relative to intrinsic point defect formation energies using the Generalized Gradient Approximation (GGA) and GGA+U approximations for the exchange-correlation interactions are reported and compared to experimental data. The GGA and GGA+U approximations yield different formation energies for both Frenkel pairs and Schottky trios, showing that the 5*f* electron correlations have a strong influence on the defect formation energies. Using GGA, various migration mechanisms were investigated for oxygen and uranium defects. For oxygen defects, the calculations show that both a vacancy and an indirect interstitial mechanism have the lowest associated migration energies, 1.2 and 1.1 eV respectively. As regards uranium defects, a vacancy mechanism appears energetically more favourable with a migration energy of 4.4 eV, confirming that oxygen atoms are much more mobile in UO_2 than uranium atoms. Those results are discussed in the light of experimentally determined activation energies for diffusion.

1. Introduction

The aim of this study is to investigate oxygen and uranium self-diffusion in uranium dioxide. Activation energies for both oxygen [1–5] and uranium [4,6,7] self-diffusion have been measured and reported in the literature, but still little is known about migration mechanisms. First-principles modelling provides a particularly useful tool for investigating migration processes at the atomic scale. The formation energies of point defects have already been studied within the framework of Density Functional Theory (DFT), especially using the so-called GGA+U approximation [8–12]. It has been shown recently, however, that the results obtained in those studies might be inaccurate due to the occurence of non-global energy minima within the GGA+U formalism [13–16]. The presence of these metastable states induces large discrepancies in the formation energies published so far. In order to obtain reliable point defect formation energies, it is therefore required to control the occupation matrices of uranium correlated orbitals in order to ensure that the ground state is reached [15,16].

In the present article, we first report formation energies calculated in GGA and GGA+U using an occupation matrix control scheme developed on the perfect crystal [15] in order to obtain the most reliable formation energies. These results are compared to other DFT results, as well as experimental data. The second part of the article focuses on the uranium and oxygen migration energies. Given the important computational resources required by GGA+U calculations, the GGA approximation is used for studying defect migration mechanisms in UO_2. The migration energies corresponding to different migration paths of oxygen and uranium defects are calculated using the Nudged Elastic Band method [17], and provide indications as to the most favourable mechanisms for the migration for these defects in the UO_2 fluorite lattice. Finally, our results are fed into a simple point defect model to derive activation energies for self-diffusion in UO_2 which are further compared to experimental data.

2. Computational method

Calculations are done within the framework of DFT [18,19] and using the Projector Augmented Wave method [20] as implemented in the Vienna Ab-initio Simulation Package (VASP code) [21–23]. The Generalized Gradient Approximation (GGA) as parametrized by Perdew, Burke and Ernzerhof (PBE) [24] is used to describe the exchange–correlation interactions. For the calculation of formation energies, a Hubbard-like term is added in order to take into account the strong correlations between the 5*f* electrons of the uranium atom, resulting in the so-called GGA+U approximation. The price to pay for this improved description, however, is the significantly increased number of energy minima (ground state + metastable states) [13–16], which makes it less straightforward to determine the ground state of the system.

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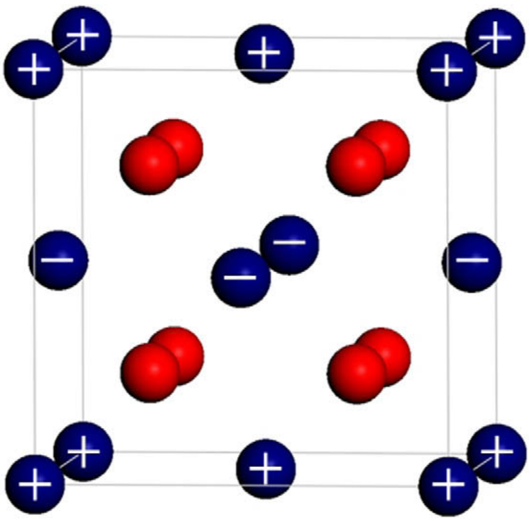

Fig. 1. UO_2 unit cell (fluorite structure) and its antiferromagnetic ordering. Uranium atoms are drawn in blue and oxygen atoms in red. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

The Liechtenstein's approach [25] of the GGA+U approximation is used in our study of defects in UO_2, with parameters $U = 4.50$ eV and $J = 0.51$ eV, as determined by Kotani and Yamazaki based on the analysis of X-ray photoemission spectra [26]. Point defects are modelled using a 96-atom supercell whose Brillouin zone is sampled by a $2 \times 2 \times 2$ Monkhorst–Pack [27] *k*-point grid. A 500 eV cut-off energy is used to truncate the plane-wave expansion of the electron basis set. These parameters ensure that total energies are converged to <25 meV per atom. Forces were also checked to be lower than 2×10^{-3} eV/Å. The spin polarization of UO_2 was taken into account both in GGA and GGA+U calculations with a 1**k** antiferromagnetic order (see Fig. 1). This antiferromagnetic configuration is an approximation of the non colinear 3**k** order seen experimentally [28], which would require too much computational time to be taken into account in our study of defects. However, according to the results of Laskowski et al. [29], the error caused by this approximation should be less than 30 meV for the $U - J$ value used in our calculations. In all calculations, atomic positions are optimized and the cell volume is kept constant.

3. Formation energies of point defects

We have calculated the formation energies of the uranium and oxygen Frenkel pairs, as well as that of Schottky trios. Frenkel pairs (FP_X) are intrinsic defects in which an interstitial element X lies near a vacancy of the same element (X = uranium or oxygen), whereas Schottky defects (S) form when two oxygen atoms and one uranium atom leave their lattice site, creating three vacancies. The formation energies for these defects are defined as follows:

$$\begin{aligned} E^{F}_{FP_X} &= E^{N-1}_{V_X} + E^{N+1}_{I_X} - 2 \times E^{N} \\ E^{F}_{S} &= E^{N-1}_{V_U} + 2 \times E^{N-1}_{V_O} - 3 \times \tfrac{N-1}{N} \times E^{N} \end{aligned} \qquad (1)$$

where E^N is the total energy of the N-atom supercell (in this study, $N = 96$), $E^{N-1}_{V_X}$ and $E^{N+1}_{I_X}$ are the total energies of the supercell with an X-type vacancy and X-type interstitial, respectively. Note that these energies are calculated using the total energies for isolated defects, *i.e.* interstitial atoms and vacancies are studied in separate supercells. It has been shown [9,11], however, that the interaction between defects have a large influence on the defect formation energies of complex point defects. We neglected this interaction between defects because one of the approximations of our model used to calculate activation energies (see Section 5) reckons that Frenkel pairs and Schottky defects are made of isolated defects. It should also be noted that the calculation of formation energies does not require an arbitrary energy reference, as is the case for single vacancies and interstitials. Results are therefore more easily comparable to experimental data [30]. The formation energies obtained in GGA (with and without spin polarization) and GGA+U are reported in Table 1.

Table 1
Formation energies (in eV) of oxygen and uranium Frenkel pairs (FP_O and FP_U, respectively) and of Schottky defects (S), calculated in the non spin polarized GGA (NSP-GGA), the spin polarized GGA (SP-GGA) and the spin polarized GGA+U (SP-GGA+U) approximations.

	NSP-GGA	SP-GGA	SP-GGA+U	Experimental [30]
FP_O	3.7	3.3	6.5	3.0–4.0
FP_U	9.0	9.3	14.6	9.5
S	4.9	4.1	10.6	6.0–7.0

We see from Table 1 that the formation energies yielded by the GGA+U approximation are much larger than those yielded by the GGA approximation. This shows that the 5*f* electrons correlations have a strong influence on the formation energies of point defects. In addition, the GGA+U values are larger than the experimental values. The main explanation for this discrepancy could be that we neglected the interaction between defects of the Frenkel pairs and Schottky trios. As mentioned above, this interaction significantly decreases the defect formation energies. Another part of the discrepancy might come from uncertainties in the experimental measurements.

In addition, using GGA+U, Iwasawa et al. [8], Gupta et al. [9], Nerikar et al. [10] and Yu et al. [12] obtained values different from those reported in this study. These apparently conflicting results reported in GGA+U calculations stem from the difficulty in obtaining the ground state [15]. Due to the significant increase in the number of metastable states in GGA+U compared to GGA, the system can often be trapped in one of these metastable states, and the energy obtained depends upon the calculation starting point. To make sure that the calculation is actually converged to the ground state, one should check the 5*f* orbital occupations with the two *f* electrons located on the two lowest orbitals. For this purpose, we used an efficient occupation matrix control scheme to calculate these formation energies and we therefore believe the ground state must have been reached for these systems. The energies calculated are therefore very probably ground state energies. Charge transfers and atomic magnetic moments were analyzed for the oxygen Frenkel pair. It is found that two neighbouring uranium atoms of the oxygen interstitial have transferred one electron each. This results in the oxygen interstitial being charged 2-while the two neighbouring uranium atoms are charged 5+.

4. Migration of oxygen and uranium point defects

The migration paths of oxygen and uranium defects were calculated using the Nudged Elastic Band method [17]. This method enables one to determine the minimum energy path of an atom between two equilibrium positions in the chosen migration direction by calculating the forces acting on the migrating atom. The relaxation of the positions of the remaining atoms of the system is also taken into account. In our calculation, the forces were computed using the GGA approximation within the DFT framework. The total energy of the system can be calculated for various intermediary migration steps and the migration energy is defined as the energy barrier along the migration path: it is the energy of the

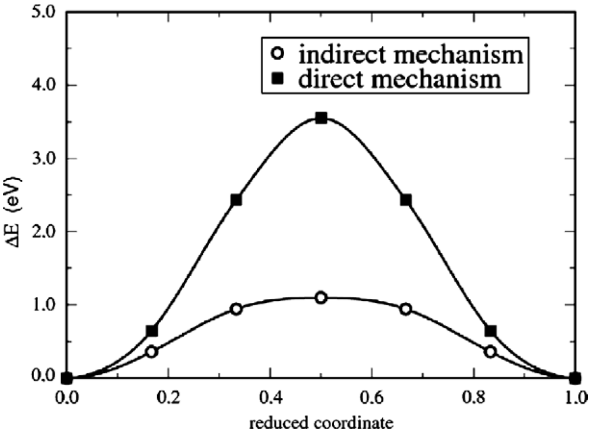

Fig. 2. Energy barriers (in eV) associated with the migration of an oxygen interstitial by a direct mechanism (full squares) and an indirect mechanism (empty circles).

Table 2
Migration energies (eV) for oxygen and uranium defects calculated for various migration mechanisms. See the text for the definition of these mechanisms.

Mechanism	Vacancy	Direct interstitial	Indirect interstitial
Oxygen	1.2	3.6	1.1
Uranium	4.4	5.8	–

system at the saddle point. In this study, we considered the migration of vacancies and interstitial atoms in association with the migration mechanisms as follows:

- A vacancy mechanism, in which an atom moves to a nearest neighbour vacancy of the same chemical specie.
- An interstitial mechanism, in which an interstitial atom in an octahedral site moves to the next nearest octahedral interstitial site.
- An indirect interstitial mechanism, in which an atom in an octahedral site replaces an atom on a lattice site, which in turn moves to an octahedral interstitial site. This mechanism is only considered for oxygen atoms.

The calculated energies along the two paths considered for the oxygen interstitials (the direct and the indirect mechanisms) are shown in Fig. 2. The maximum of these energy curves, *i.e.* the migration energies, are reported in Table 2, for the oxygen and uranium sublattices.

We find that the lowest migration energies are obtained for oxygen defects, which confirms that oxygen is more mobile than uranium in UO_2. For oxygen defects, among the different migration mechanisms investigated, we find that both the vacancy and indirect interstitial mechanism are the most favourable, with a migration barrier of only 1.2 eV and 1.1 eV, respectively. For uranium defects, the vacancy mechanism has the lowest migration energy: 4.4 eV.

5. Discussion

The difficulties in ascertaining whether the calculated data are at all relevant are numerous. Firstly, to our knowledge, no direct reliable experimental determination of defect migration or formation energies exists for UO_2. This is hardly surprising considering the many difficulties involved in determining such values [31]. For instance the cation vacancy and interstitial migration energies as determined by Soullard et al. [32] through electron irradiation of thin UO_2 foils was evaluated at roughly 2 eV and 0.3 eV respectively, in contrast to the values obtained in this study of 4.4 eV and 5.8 eV. The alternative therefore is to trust self-diffusion activation energies and compare the experimental data relative to diffusion measurements to the theoretical values obtained from the energies calculated using *ab initio* methods, *via* a thermodynamic model. The simplest of these models, proposed by Lidiard [33] and Matzke [31], is based on mass action equations involving point defects. A number of postulates underpin this model. The first and most important is that the material is subject to Frenkel and Schottky disorder only. In effect therefore, only point defects on the anion and cation sublattices are treated. Note also that the point defect model was purposefully chosen so that the energies it required, calculated using the atomistic model, did not require choosing a necessarily arbitrary reference state. We have looked at the predicted activation energies for diffusion in stoichiometric UO_2 obtained using the GGA calculated formation (Table 1, 1st column) and migration energies (Table 2). The usual simplifying hypotheses were made in order to produce simple expressions for the point defect concentrations on each sub-lattice. The activation energies obtained assuming an interstitial or a vacancy assisted mechanism are then compared to the experimental data available. This comparison is indicated in Table 3.

Table 3
Comparison of experimental and theoretical activation energies (in eV) for oxygen and uranium self-diffusion.

	Vacancy (theoretical)	Interstitial (theoretical)	Experimental [3]
Oxygen	2.8	3.2	2.5
Uranium	6.0	13.2	3.8–5.6

The analysis of this data shows two very encouraging features for stoichiometric UO_2:

- The theoretical results are very much in line with the best available experimental data, within experimental uncertainties and scatter amongst the various studies. This type of agreement has never, to our knowledge, been demonstrated.
- Agreement exists between experiment and theory both for the anion and cation sublattices.

6. Conclusion

We have studied the formation energies of uranium and oxygen Frenkel pairs, as well as of Schottky defects. To ensure that the ground state is reached within GGA+U calculations, we use an efficient occupation matrix control scheme developed on bulk UO_2. We found that GGA+U gives results larger than GGA and experimental data available for the oxygen Frenkel pair and the Schottky defect. This points out that the correlation term of the Hamiltonian, describing interactions between 5*f* electrons, has a strong influence on the point defect formation energies. We have also shown that GGA calculations find the most favourable migration mechanisms for an oxygen defect in stoichiometric UO_2 to be a vacancy and an indirect interstitial mechanism. For the uranium defect a vacancy mechanism appears to be more favourable than an interstitial one. This study is being completed by GGA+U calculations of the migration energies to confirm these results. The GGA+U will also allow us to study charged defect migration mechanisms. In addition, use of a simple thermodynamic model based on mass action equations describing Frenkel and Schottky disorder has enabled us to assess migration and formation energies obtained in GGA against experimental self-diffusion activation energies. Results show very encouraging features and this approach is being extended to hyper- and sub-stoichiometric composition ranges of UO_{2+x}. Such an approach for the study of the stability and the mobility of point defects will be extended in the future to an other class of nuclear fuel materials, namely uranium and plutonium carbides.

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