Computer simulation of defect clusters in UO2 and their dependence on composition

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HIGHLIGHTS
• Edge-sharing 2:2:2 Willis cluster chains most stable defects in UO2.125 and UO2.25.
• Unstable relative to split di-interstitial cluster at UO2.0625.
• More stable than competing defects (cuboctahedra/split-interstitials) at UO2.125.
• U5+ predicted as charge compensating species.
• Defect behaviour dictated by stoichiometry/composition.

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ABSTRACT

It is recognised that point defects play a key role in the behaviour and properties of many technologically significant oxides. What is less well understood is how these defects cluster together and, crucially, the extent to which the clusters change with composition. We chose to investigate this phenomenon by considering UO2, a nuclear fuel material for which there is contradictory data in the literature concerning defect clustering as a function of oxygen content. Early studies of fluorite UO2+ x proposed a model based on 2:2:2 Willis clusters whilst more recent research suggests cuboctahedral or split quad-interstitial defect clustering. Here we use the PBE + U functional to simulate defective UO 2+ x and find for 0.125 < x < 0.25, chains of edge-sharing 2:2:2 Willis clusters to be most stable. Below x = 0.125 these chains destabilise, transforming in to split di-interstitial clusters, demonstrating that the type of oxygen cluster present is dependent on local environment and stoichiometry.

1. Introduction

UO2 is one of the most important materials in the nuclear fuel cycle, forming the primary fuel component in most nuclear reactors worldwide. Although it adopts the fluorite structure it is easily oxidised, particularly under reactor operating conditions, and exhibits complex anion defect behaviour. An intricate knowledge of the properties of hyperstoichiometric UO2 and the impact of excess oxygen on the materials stability and performance are crucial. As such oxygen defects in UO2 are a well-known phenomenon that has been the subject of considerable experimental [1–5] and computational research [6–12].

The first hyperstoichiometric UO2 model was derived from the neutron diffraction measurements of Willis [1–3] that suggested oxygen interstitials (Oi) do not occupy the octahedral site at the centre of oxygen sub-lattice cubes but rather occupy two positions displaced approximately 1 Å from the octahedral site along (110) and (111) directions, designated O′ and O″, respectively (Fig. 1(a)). These findings led Willis to propose a clustering model under which these Oi aggregate, now referred to as Willis clusters [13]. The foremost of these complexes is the 2:2:2 cluster, named for the combination of two O′ interstitials, two O vacancies (VO) and two O″ interstitials. Periodic chains of isolated 2:2:2 clusters were later used to rationalise the structures of the fluorite based uranium oxides U4O9 and U3O7 (both defective fluorite-based materials) by Allen et al. [4,5]. The more recent study of Bevan et al. [14] proposed the cuboctahedral cluster (COT-12) as a structural feature of U4O9. This cluster is formed of eight VO (a vacant oxygen sub-lattice cube) replaced by 12 Oi (in a cuboctahedron) (Fig. 1(c)). This result was supported by the work of Desgranges et al. [15], and has subsequently been considered as a defect arrangement in UO2+. Most recently He et al. reported the COT-12 cluster to dominate in U4O9, whilst 2:2:2 Willis clusters...
and point interstitials form at lower stoichiometries (UO$_{2.15-2.3}$ and UO$_{2.00-2.05}$) [16].

The early theoretical work of Catlow assessed a number of Wil-\[is type clusters and found them all to be stable using potential-based methods [6]. More recently “split interstitial” type clusters (Fig. 1) have emerged from computational studies as stable species following the potential based investigation of Govers et al. which found the 2:2:2 cluster in a UO$_2$ supercell relaxed to a split di-interstitial [13] (Fig. 1(b)); a single VO with three O$_i$ displaced approximately 1.6 Å in (1 1 1) directions from the VO$_i$. This result was later confirmed by the LSDA + U calculations of Geng et al. [7]. The family of split interstitial clusters was extended to include tri-interstitials [8] (a di-interstitial with the fourth O$_i$ site occupied) and quad-interstitials [9] (two di-interstitials on adjacent sites, giving a total of two VO$_i$ and six O$_i$) (Fig. 1(d)). Following this Andersson et al. postulated a model for U$_4$O$_9$ based on a UO$_2$ supercell containing multiple split quad-interstitial clusters; following the prediction of their LSDA + U calculations that the quad-interstitial is more stable than its cuboctahedral counterpart [12].

Thus despite renewed interest in UO$_{2+x}$, U$_4$O$_9$ and U$_3$O$_7$ there is still considerable debate over their structures. Experimentally this is due in no small part to the difficulty in distinguishing defect signals from supercell-related peaks whilst computationally the unit cells can be prohibitively large to simulate with DFT [12].

Here we present our recent simulations, including U$_4$O$_9$ stoichiometry phases based on defective UO$_2$ supercells. Starting from a 48 atom UO$_2$ supercell ($1 \times 2 \times 2$) we examine all 33 symmetry inequivalent arrangements of four O$_i$ and all 11 unique

![Fig. 1. Relaxation of a 2:2:2 Willis cluster (a) to a split di-interstitial cluster (b), (c) shows a 12 atom cuboctahedral cluster and (d) is a split quad-interstitial cluster. Black spheres represent U ions, red indicate fluorite O ions, blue designate O$_i$ and green represent VO$_i$. Bonds have been drawn in (a) and (c) between O$_i$ and in (b) and (d) between O$_i$ and VO$_i$ to highlight the cluster geometries. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

![Fig. 2. Plot showing predicted formation energies for each calculated U$_4$O$_9$ phase (diamonds) and change in volume relative to UO$_2$ per uranium ion (crosses). Purple markers indicate one or more U(VI) ions were predicted for that system. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)](image-url)
configurations of two di-interstitial clusters, both having U₄O₉ stoichiometry. Then the most stable configuration from these simulations is placed in a 2/C₂/C₂U/O₂ supercell (96 atoms) to produce UO₂.125 and UO₂.0625 systems, allowing us to examine a greater range of stoichiometries and how overall phase composition affects defect cluster stability.

2. Methodology

All calculations were performed using PAW pseudo-potentials and the GGA in VASP[17] with the PBE + U functional[18]. The Dudarev scheme[19] (U = 4.5 eV, J = 0.54 eV[20]) and a plane-wave cutoff energy of 400 eV were employed. 4/C₂/C₂ k-point meshes were used for U₄O₉ (48 atoms) and 2/C₂/C₂ grids for UO₂.125 and UO₂.0625 systems (96 atoms). These cutoff and k-point settings are in accordance with previous DFT studies[7,9]. Convergence criteria for electronic and ionic relaxation schemes were 1×10⁻⁶ eV/atom and 0.01 eV/Å respectively. This methodology is consistent with previous studies of defects in UO₂[8,9]. Symmetry inequivalent defect configurations were identified using the site-occupancy disorder (SOD) program[21] and all calculations used 1k antiferromagnetic (AFM) ordering, considered to be an appropriate approximation for the experimentally observed 3k noncollinear AFM ordering[22,23].

The formation energies of the defective phases relative to UO₂ were calculated by subtracting the predicted oxygen chemical potential (−4.93 eV/O ca. exp. −5.1 eV/O[24]) from the VASP calculated total energy, in accordance with comparable studies in the literature[8,9,12]. All formation energies are expressed per excess O introduced.

3. Results and Discussion

The U₄O₉ simulation results predict a number of different defect configurations over a wide range of stability with some common characteristics amongst the most and least stable systems. Fig. 2 is a plot of formation energy and volume change for each U₄O₉ system. Table 1 shows formation energies and defect configurations of selected simulations. Stability is related to the amount of O bound in clusters compared to the amount of isolated O(Fig. 2). We found that a single 2:2:2 Willis cluster (UO₂.0625) relaxes to a split di-interstitial cluster, as reported by Govers et al.[13], Geng et al.[7], Andersson et al.[25] and Wang et al.[26]. However, we found that the most stable U₄O₉ configurations contain a single or double chain of 2:2:2 Willis clusters suggesting only groups of Willis clusters are stable at particular local stoichiometries. Wang et al. report the O/O' ratio is consistent with Willis clusters at UO₂±1 stoichiometry, however split-interstitial type clusters dominate the UO₂±0.5 region with the Willis cluster representing a transition state.

| Stoich | Figs. | Config | \( \Delta E_{\text{formation}} \) (eV) | \( \Delta V \) (%)
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<tr>
<td>UO₂.25</td>
<td>3(d)</td>
<td>4 × O₉</td>
<td>0.49</td>
<td>1.14</td>
</tr>
<tr>
<td>UO₂.25</td>
<td>3(c)</td>
<td>2:2:2/2 × O₉</td>
<td>0.18</td>
<td>0.93</td>
</tr>
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<td>2:2:2 chain</td>
<td>0.52</td>
<td>0.68</td>
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<tr>
<td>UO₂.25</td>
<td>3(a)</td>
<td>2:2:2/2 chain</td>
<td>0.53</td>
<td>0.16</td>
</tr>
<tr>
<td>UO₂.125</td>
<td>3(a) + UO₂ bulk</td>
<td>2:2:2 chain</td>
<td>0.68</td>
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<td>UO₂.125</td>
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<td>UO₂.0625</td>
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Fig. 3. Relaxed U₄O₉ phases (a) a double 2:2:2 Willis cluster chain, (b) a single 2:2:2 Willis cluster chain, (c) a single distorted 2:2:2 Willis cluster and (d) four isolated O. Colour is the same as Fig. 1 with the addition of yellow and purple spheres to represent U (V) and U (VI) ions respectively. To highlight the 2:2:2 clusters bonds have been drawn between their constituent oxygen ions. The “peroxide” O have been circled in (c). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
Of the 44 U4O9 systems almost half relaxed to a configuration involving edge-sharing 2:2:2 cluster chains (most stable), a quarter relaxed to four isolated O8 (least stable) and the remainder to combinations of split interstitial clusters and isolated O9 (intermediate stability). Distorted 2:2:2 Willis cluster chains were less stable than undistorted; the distorted chains being comparable in stability to undistorted split-interstitial based systems. The stable, undistorted 2:2:2 cluster chains all align in (100) directions linked by edge-sharing (Fig. 3), similarly to the chains reported by Allen et al. [5].

There is moderate correlation (r = 0.63) between U4O9 stability and volume change relative to UO2; the least stable systems generally show a volume decrease whilst the most stable increase. Consequently with applied pressure we would predict Willis chains to destabilise and O8 to become the favoured defect arrangement.

Once 2:2:2 Willis cluster chains were identified as stable entities at the U4O9 stoichiometry we sought to isolate chains (and individual clusters) at lower oxygen stoichiometries by generating 2 × 2 × 2 U2O4 supercells with stoichiometries of UO2.125 and UO2.0625. In the UO2.125 simulation the chains retained their geometry and were still predicted to be a stable defect arrangement. This is in accordance with Willis’ initial observations of the cluster from UO2.13 stoichiometry up [1]. The arrangement was almost identical to that found in the U3O8 structure, retaining the cluster chains, implying these are necessary to stabilise the cluster. To lower the stoichiometry to UO2.0625 we removed two oxygen ions from the UO2.125 cell (breaking the cluster chain to give only two edge-sharing 2:2:2 clusters). This is in fact the minimum stoichiometry (in a 2 × 2 × 2 U2O4 supercell) possible to create a 2:2:2 cluster as it contains only two O8 however the system relaxed to a split di-interstitial cluster, as previously reported [7,13,25]. The formation energies of these defects are in Table 1 and the Willis-based UO2.125 systems are found to be more stable than the equivalent cuboctahedral and split quad-interstitial containing cells (Fig. 1(c) and (d)).

Stability of the U4O9 phases is also related to the species that compensate the additional charge introduced by O8. In all simulations this is oxidation of U (IV); the vast majority of which is to U (V) however in five of the least stable configurations (Eform = 0.11–0.44 eV) one or two U (VI) ions are also predicted. Fig. 2 highlights which systems contain U (VI) and Fig. 3 shows the distribution of U (V) and (VI) in four different systems. Where there are cluster chains oxidised uranium ions tend to be in close proximity (Fig. 3(a) and (b)). One of the U (VI) containing phases also features a single distorted 2:2:2 cluster with an adjacent O9 (Fig. 3(c)). We have attributed the low stability of this configuration to the presence of an O9 only 1.443 Å from a 2:2:2 cluster O8, preventing formation of a chain by distorting the local oxygen sub-lattice. This short O-O bond is indicative of a peroxide ion (O2- 2), previously predicted by Andersson et al. in their DFT study of UO2 oxidation [12]. The prediction of U4O9 containing only U (IV) and U (V) ions is supported by the experiments of Kvashnina et al. who reached the same conclusion using x-ray absorption near edge structure (XANES) spectroscopy [27].

The coordination at U (V) and U (VI) sites adjoining 2:2:2 clusters (Fig. 4) both differ significantly from the parent fluorite lattice. U (V) sites retain a coordination number of eight but the 2:2:2 cluster significantly distorts their coordination sphere and slightly lowers the average U–O bond length to 2.294 Å from 2.368 Å. Observing Fig. 4(a) the four in-plane oxygen ions on the left show half of an oxygen sub-lattice cube (aligned in the (011) plane) whilst the other four form a flattened tetrahedron. At U (VI) sites a larger local distortion to the oxygen sub-lattice results in further reduction of the average U–O bond length to 2.188 Å and the emergence of two shorter, collinear “uranil” type bonds (Fig. 4(b)). The coordination is a puckered pentagonal bipyramid and when considered with the non-symmetrical uranyl-type bonds the U (VI) site is strongly reminiscent of the η-UO3 polymorph which also contains these structural features [28,29]. The prediction that U (VI) is unstable in U4O9 systems demonstrates the preference of U (VI) ions for layered-type structures (e.g. U3O8 and UO3) [27].

We have also computed the electronic band gaps for each phase discussed here, finding the most stable U4O9 systems (i.e. those containing 2:2:2 cluster chains) to have band gaps between 1.48 and 1.61 eV. The UO2.125 system was found to have a lower band gap of 1.38 eV and UO2.0625 lower again at 1.29 eV. Although no experimental measurements of the U4O9 band gaps could be found our result compares favourably with the LSDA + U calculated value of 1.68 eV from He et al. [30]. Given the paucity of data available in this area further investigation is warranted before we can draw any conclusions.

4. Conclusions

In summary, we investigated defective fluorite supercells with a range of stoichiometries and found for U4O9 and UO2.125 there are stable configurations of edge-sharing 2:2:2 Willis cluster chains. Reducing the stoichiometry to UO2.125 we find that these chains are retained as the defect cluster remains present in accordance with the original observations of Willis. Further reduction of the stoichiometry to UO2.0625 (a single 2:2:2 Willis cluster or two edge-sharing ones in a 2 × 2 × 2 U2O4 supercell) leads to formation of a split di-interstitial cluster in line with previous calculations. Therefore we propose that the 2:2:2 Willis cluster is a genuine feature of UO2x4 but its formation is dependent on oxygen content and...
it is only stabilised in edge-sharing chains, as reported by Allen et al. [5]. U(V) ions are predicted as charge compensating species for the oxygen defects, supporting observations that (VI) is not a stable oxidation state for U in $\text{U}_4\text{O}_9$. Having identified the oxygen concentration dependence of defects over $\text{UO}_2.0625$–$2.25$, it would be pertinent to extend the investigation to a broader range of stoichiometries; and indeed examine the extent to which defect cluster formation is dependent on oxygen stoichiometry for other materials that show mixed oxidation states. A suitable extension to this work would be including additional layers of complexity such as alternative magnetic orderings, spin orbit coupling and multiple $f$ orbital occupations. Recent studies from Dorado et al. [31] and Allen and Watson [32] have demonstrated that occupational matrix control can be used to locate the global minimum of the system, avoiding the occurrence of metastable states.

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**References**