Computer simulation of defect clusters in UO$_2$ and their dependence on composition

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**Highlights**
- Edge-sharing 2:2:2 Willis cluster chains most stable defects in UO$_2$.125 and UO$_2$.25.
- Unstable relative to split di-interstitial cluster at UO$_2$.0625.
- More stable than competing defects (cuboctahedra/split-interstitials) at UO$_2$.125.
- U$_{5+}$ predicted as charge compensating species.
- Defect behaviour dictated by stoichiometry/composition.

**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 UO$_2$, 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 UO$_{2+x}$ 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.

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**1. Introduction**

UO$_2$ 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 UO$_2$ and the impact of excess oxygen on the materials stability and performance are crucial. As such oxygen defects in UO$_2$ are a well-known phenomenon that has been the subject of considerable experimental [1–5] and computational research [6–12].

The first hyperstoichiometric UO$_2$ model was derived from the neutron diffraction measurements of Willis [1–3] that suggested oxygen interstitials (O$_i$) 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$, respectively (Fig. 1(a)). These findings led Willis to propose a clustering model under which these O$_i$ 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$,_0$ interstitials (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 UO$_2$. Most recently He et al. reported the COT-12 cluster to dominate in U$_4$O$_9$, 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- lis 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 $\langle 111 \rangle$ directions from the VO. 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 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 sig- nalı̇s 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$_9$ stoichiome- try 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
configurations of two di-interstitial clusters, both having U₄O₉ stoichiometry. Then the most stable configuration from these simulations is placed in a \( \frac{2}{C_2} \times \frac{2}{C_2} \) 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. \( \frac{4}{C_2} \times \frac{2}{C_2} \) k-point meshes were used for U₄O₉ (48 atoms) and \( \frac{2}{C_2} \times \frac{2}{C_2} \) 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 \( 1 \times 10^{-6} \) 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 UO₂.11-2.13 stoichiometry, however split-interstitial type clusters dominate the UO₂⁺ region with the Willis cluster representing a transition state

<table>
<thead>
<tr>
<th>Stoich</th>
<th>Figs.</th>
<th>Config</th>
<th>( E_{\text{formation}} ) (eV)</th>
<th>( \Delta \text{Vol} ) (%)</th>
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<tbody>
<tr>
<td>UO₂.25</td>
<td>3(d)</td>
<td>( 4 \times O )</td>
<td>0.49</td>
<td>-1.14</td>
</tr>
<tr>
<td>UO₂.25</td>
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<td>( 2:2:2/ \times O )</td>
<td>0.18</td>
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<td>3(a)</td>
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<tr>
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<td>( 2:2:2 ) chain</td>
<td>-0.53</td>
<td>0.16</td>
</tr>
<tr>
<td>UO₂.25</td>
<td>3(a) + UO₂ bulk</td>
<td>( 2:2:2 ) chain</td>
<td>-0.68</td>
<td>0.32</td>
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<tr>
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<tr>
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<td>1(d)</td>
<td>quad</td>
<td>-0.55</td>
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<tr>
<td>UO₂.0625</td>
<td>1(b)</td>
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<td>-0.97</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 O9 (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 (1 0 0) 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 \( U_4O_9 \) stability and volume change relative to \( UO_2 \); 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 \( O_9 \) to become the favoured defect arrangement.

Once 2:2:2 Willis cluster chains were identified as stable entities at the \( U_4O_9 \) stoichiometry we sought to isolate chains (and individual clusters) at lower oxygen stoichiometries by generating \( 2 \times 2 \times 2 \) \( UO_2 \) supercells with stoichiometries of \( UO_2.125 \) and \( UO_2.0625 \). In the \( UO_2.125 \) 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 \( UO_2.13 \) stoichiometry up [1]. The arrangement was almost identical to that found in the \( U_4O_9 \) structure, retaining the cluster chains, implying these are necessary to stabilise the cluster. To lower the stoichiometry to \( UO_2.0625 \) we removed two oxygen ions from the \( UO_2.125 \) cell (breaking the cluster chain to give only two edge-sharing 2:2:2 clusters). This is in fact the minimum stoichiometry (in a \( 2 \times 2 \times 2 \) \( UO_2 \) supercell) possible to create a 2:2:2 cluster as it contains only two \( O_9 \), 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 \( UO_2.125 \) 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 \( U_4O_9 \) phases is also related to the species that compensate the additional charge introduced by \( O_9 \). 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 (\( E_{\text{form}} = 0.11–0.44 \) 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 \( O_9 \) (Fig. 3(c)). We have attributed the low stability of this configuration to the presence of an \( O_9 \) only 1.443 Å from a 2:2:2 cluster \( O_9 \), preventing formation of a chain by distorting the local oxygen sub-lattice. This short \( O-O \) bond is indicative of a peroxide ion (\( O_2^2- \)), previously predicted by Andersson et al. in their DFT study of \( UO_2 \) oxidation [12]. The prediction of \( UO_9 \) containing only \( U(IV) \) and \( U(V) \) ions is supported by the experiments of Khvasha 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 (0 1 1) 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 “uranyl” 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 \( \eta \)-\( UO_3 \) polymorph which also contains these structural features [28,29]. The prediction that \( U(VI) \) is unstable in \( U_4O_9 \) systems demonstrates the preference of \( U(VI) \) ions for layered-type structures (e.g. \( U_5O_8 \) and \( UO_3 \)) [27].

We have also computed the electronic band gaps for each phase discussed here, finding the most stable \( U_4O_9 \) systems (i.e. those containing 2:2:2 cluster chains) to have band gaps between 1.48 and 1.61 eV. The \( UO_2.125 \) system was found to have a lower band gap of 1.38 eV and \( UO_2.0625 \) lower again at 1.29 eV. Although no experimental measurements of the \( U_4O_9 \) 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 \( U_4O_9 \) and \( UO_2.125 \) there are stable configurations of edge-sharing 2:2:2 Willis cluster chains. Reducing the stoichiometry to \( UO_2.125 \) 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 \( UO_2.0625 \) (a single 2:2:2 Willis cluster or two edge-sharing ones in a \( 2 \times 2 \times 2 \) \( UO_2 \) 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 \( UO_{2+x} \) 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 $U_4O_9$. Having identified the oxygen concentration dependence of defects over $UO_{2.0625–2.25}$ 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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