**Ab initio** investigation on oxygen defect clusters in UO$_{2+x}$

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By first-principles LSDA+U calculations, we revealed that the current physical picture of defective uranium dioxide suggested solely by neutron diffraction analysis is unsatisfactory. An understanding based on quantum theory has been established as a thermodynamical competition among point defects and cuboctahedral cluster, which naturally interprets the puzzled origin of the asymmetric O$^\prime$ and O$''$ interstitials. It also gives a clear and consistent agreement with most available experimental data. Unfortunately, the observed high occupation of O$''$ site cannot be accounted for in this picture and is still a challenge for theoretical simulations.

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Fluorite structure commonly appears in rare earth and actinide oxides. One of them UO$_2$ is the nowadays widely adopted nuclear fuel and most of whose applications are highly related to atomic defect behaviors. The current physical picture of defective UO$_2$ is based purely on neutron diffraction measurements. It suggested that no oxygen can occupy the octahedral site (O$_h$) of the cation FCC lattice and all oxygen interstitials should displace from this site along the ⟨110⟩ and ⟨111⟩ directions about 1 Å (sites O$'$ and O$''$), respectively, to form the so-called Willis type clusters by associating with the nearby oxygen vacancies (O$_v$).\[1,2,3,4]\ Note the clustering interpretation in this picture is suggestive and might be ambiguous since explicit atomic positions are unavailable in those experiments. But this suggestion invalidated the point defect model and diffusion mechanism that widely employed to describe fuel behaviors.\[5,6,7]\ Also it itself is inconsistent in that it requires a quite different cuboctahedral (COT) cluster to account for the closely related U$_4$O$_9$/U$_3$O$_7$ phase.\[2,8,9,10,11,12]\ This situation provoked confusion because it is difficult to investigate the Willis clusters thoroughly and meanwhile people are unsure how large the clustering effects should be.\[7,13,14,15,16]\  

On the other hand, as a powerful quantum mechanics technology, density functional theory provides an accurate \textit{ab initio} method to understand material behaviors.\[17\] For example the bulk stoichiometric UO$_2$ has been well described by local density approximation with Hubbard correction (LSDA+U) functional.\[19\] Application of this method to non-stoichiometric UO$_{2+x}$ also showed amazing agreement with available experiments, namely, in (i) negative volume change induced by oxygen interstitials, (ii) predominance of oxygen defects when \(x > 0\), (iii) exclusive COT clusters at high \(x\) region (U$_4$O$_9$/U$_3$O$_7$).\[1,2,3,4,5,6,7,8,9,10,11,20\] In this letter we will investigate the full temperature-composition region to study the oxygen defect clustering behaviors in UO$_{2+x}$ with this method.

All defects were modeled in a \(2 \times 2 \times 2\) fluorite cubic cell with otherwise 96 atoms. Larger supercells also tried to check the size effect. Structure optimization has been performed with P1 symmetry and until all forces and stress less than 0.01 eV/Å. The employed computational technique and parameters, such as the kinetic energy cutoff and sampling k-points, are the same as in Ref.\[7\].

![FIG. 1: Relaxation process of the Willis 2:2:2 cluster (a) to a V-3O$'$ split interstitial (b): each cube indicates one oxygen cage and the solid arrows point to atomic relaxation directions; in (a) the topside interstitial will annihilate the nearest vacancy eventually and the two O$'$ interstitials move downwards to the nearby O$''$ sites.](image)

Willis-type cluster has a geometry of that O$'$ interstitials pushing the nearest lattice oxygen displaced along the ⟨111⟩ direction and thus created a connected O$'$:O$''$ defect cluster.\[2,8\] A typical 2:2:2 cluster is shown in figure 1(a). Other already suggested clusters include 1:2:2, 4:3:2, 2:3:2 and so on.\[13\] We have checked the structural stability of several simple clustering models in Ref.\[7\], but failed to give a definite conclusion for Willis clusters due to the limitation of the method employed there. Here we will investigate the stability of 1:2:2, 2:2:2 and 3:3:2 (with 2 inequivalent configurations,
but failed to find any evidence that they were favored. We have tried several primary calculations on big clusters ranged interaction that can stabilize the structure. For clusters bigger than 4:3:2, there is no long-
uranium vacancy, COT-o, V
and themselves then relaxed to O
directions. Figure 1(b) gives the final configuration, showing that Willis-type cluster is not even metastable.
In details, all 1:2:2 clusters relaxed to a point oxygen interstitial in fact cannot push the nearest lattice oxygen out along the ⟨001⟩ direction. Instead itself will relax to an O′ site to form a split-interstitial (V-30′′/V-40′′) or to annihilate nearby vacancy. This is different from that in COT clusters where the integral support stabilizes the O′ interstitials.[21] In the case of 2:2:2, the topside O′ will annihilate the nearest O, with a little distortion along the ⟨111⟩ direction; the two O’s will move downwards to the nearest O′ sites and form a V-30′′ cluster with the low O′ interstitial. This rule applies to other Willis clusters too. For example, In 1:2:2 and 2:3:2 cases, O′ interstitials were not capable of supporting the structure and all interstitials annihilated nearby vacancies with the last one relaxed to an O1 site; the four O’s in 4:3:2 also could not prevent the O′s from annihilating and themselves then relaxed to O′ positions surrounding the middle vacancy and formed a V-40′′ cluster.

This makes the concept of Willis cluster generally failed. For clusters bigger than 4:3:2, there is no long-ranged interaction that can stabilize the structure. We have tried several primary calculations on big clusters but failed to find any evidence that they were favored.

Since all Willis-type clusters will relax to O1, V-30′′, V-40′′ and their combinations, it is reasonable to assume that V-30′′ and V-40′′ clusters might take the role of Willis clusters to account for the measured occupation number of O′ and O″ sites.[2 3] To verify this assumption, we calculated these two clusters in a 2 × 2 × 2 supercell. The defect induced volume changes and energetic information are listed in Table I. Like O1 and COT clusters, V-30′′ and V-40′′ clusters all result in a negative volume change, but is much smaller than that of COT-o (COT with one O″ occupies the center).[7, 20]

As suggested by counting the nearest vacancy-interstitial pairs, V-40′′ has lower overall and per excess oxygen formation energies. But due to the number of Frenkel pair available when compensating with point O, the formation energy per Frenkel pair of V-40′′ is a little higher than that of V-30′′.

The defect concentrations as a function of temperature and composition x were calculated with the independent clusters approximation.[5, 20] This method is exact at low temperatures low defect concentrations where atomic vibrational effects and correlation among defect clusters are negligible. Under the constraint of $x = 2(|V_f| - |V_o|) + \sum_j n_j \rho_j + 2 \sum_i n_i \rho_i - 2|V_o|$ where i runs over COT-v and COT-o clusters and j over V-30′′ and V-40′′ (with n is the excess number of oxygen in each cluster, and the coefficient 2 before the second summation arises from the fact that these clusters are defined on the oxygen sublattice), we then got the defect concentrations by Eq.(1) of Ref.[20] in the closed regime where no particle-exchange with the exterior occurs.

The results at 1500 K are shown in Figure 2, where all unshown defect concentrations are small enough to be ignored. Cluster V-30′′ and V-40′′ compete each other throughout the whole x region, while their concentrations are always 1 order smaller than uranium vacancy and 2 orders smaller than that of O1 and COT-o. At lower temperatures their concentrations reduce further, and can be neglected.

In this way a physical picture about oxygen defects appears, i.e., the nontrivial oxygen interstitials in hyper-stoichiometric regime are only O1 and COT-o. All O′ and O″ should come from COT-o clusters. This picture describes very well the high x region where U1O9/U3O7 dominated. It also explains the origin of asymmetric O′ and O″ interstitials and the non-negligible O, at T~ 300 K and x ~ 0.1 qualitatively. However, it left

| x       | ΔV (Å³) | E_f (eV) | E_vf (eV) | E_vf (eV) |
|---------|---------|----------|-----------|-----------|
| V-30′   | 0.25    | −0.21    | −3.88     | −1.94     | 3.72      |
| V-40′   | 0.25    | −0.42    | −6.74     | −2.25     | 3.96      |
a quantitative discrepancy: the experimental occupation number of O′ and O″ is 0.08:0.16 (which had been corrected to 0.13:0.12 late[3]), 0.14:0.12, and 0.33:0.10[4] when x at around 0.11–0.13. It evidently asks for a low O′:O″ ratio, but COT-o cluster can provide only a ratio of 12:1. [20]

This disagreement is unlikely due to the failure of the current model. Three independent measurements on U3O8 and U4O7 has definitely proved that the clusters in these phases are COT exclusively, i.e., the O′:O″ ratio should approach to 12:1 at high x region. Meanwhile, the monotonicity of defect concentrations vs x is insensitive to the exact formation energies. It seems impossible that V-3O′/V-4O″ cluster (contributor to O″) would have a considerable concentration at x ≈ 0.11 but disappear at a higher one. However, the possible decomposition/reassembly of COT clusters might have some impact on this issue, and we look forward to some understanding from this aspect.

On the experiment side, ambiguity existed in its post data analysis. Recall the correction of the O′:O″ ratio from 0.08:0.16 to 0.13:0.12[2, 3] and the similar vagueness in U3O8/U4O7 about the position of the center oxygen in COT clusters. [5, 6, 10, 20] we know it is very difficult to extract the explicit atomic geometry from powder neutron diffraction measurements, especially for UO2+x that is not an ordered phase and some peaks were broadened drastically. Another cause that might affect the O′ occupation is oxygen partial pressure. If experiment were performed in an open atmosphere and the powder were fine enough, then the above model need to be revised to take oxygen-exchange with the exterior into account. Then the defect concentration becomes proportion to \[ \rho_i \sim \exp \left( \frac{-E_i}{k_B T} \right) (P_o f(T))^{n_i/2} \] where oxygen partial pressure \( P_o \) could modify the concentration of V-3O′/V-4O″ cluster greatly. Anyway, it requires more endeavor from theorist and experimentalist to remove this discrepancy.

In summary we clarified the defect clustering structure in UO2+x by first principles calculations. The Willis clusters have been proved generally failed. A picture of oxygen defective UO2 was established based on thermodynamical competition between O1 and COT-o cluster, which explains most available experiments very well. The last confusion is about the role of O1 in UO2+x, Willis once argued that oxygen should not occupy this site based on his observations. [1, 2] Above discussion indicated this argument is inappropriate. In order to explain the Willis’ observation that O1 is negligible we should take the effect of temperature and composition into account. Using the calculated defect concentrations, we plotted a pseudo phase diagram for oxygen defects in UO2+x, as shown in figure 3. Note each COT-o cluster contributes 13 single oxygen interstitials and the figure was plotted according to which kind of interstitial is majority (from O1 or from COT-o). The figure clearly illustrated the predominant region of O1 is at low x and high temperatures. Mind all experiments available so far were conducted in the region marked by the hatched area, [2, 3, 4] which is far from the O1 territory. It is then understandable why experiments failed to detect O1.

FIG. 3: Pseudo phase diagram for oxygen interstitials in UO2+x, where the hatched area marks the region in which the neutron diffraction measurements performed.

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