Point defects and clustering in uranium dioxide by LSDA+U calculations

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A comprehensive investigation on point defects and their clustering behavior in nonstoichiometric uranium dioxide UO$_{2+x}$ is carried out using LSDA+U method based on density functional theory. Accurate energetic information and charge transfers available so far are obtained. With these energies that have improved more than 50% over that of pure GGA and LDA, we show the density functional theory predicts the predominance of oxygen defects over uranium ones at any compositions, which is possible only after treated the localized 5f electrons properly. Calculations also suggest an upper bound of $x \sim 0.03$ for oxygen clusters to start off. The volume change induced by point uranium defects is monotonic but nonlinear, whereas for oxygen defects, increase $x$ always reduces the system volume linearly, except dimers that require extra space for accommodation, which has been identified as meta-stable ionic molecule. Though oxygen dimers usually occupy Willis O'' sites and mimic a single oxygen in energetics and charge state, they are rare at ambient conditions. Its decomposition process and vibrational properties have been studied carefully. To obtain a general clustering mechanism in anion-excess fluorites systematically, we also analyze the local stabilities of possible basic clustering modes of oxygen defects. The result shows an unified way to understand the structure of Willis type and cuboctahedral clusters in UO$_{2+x}$ and $\beta$-U$_4$O$_9$. Finally we generalize the point defect model to the independent clusters approximation to include clustering effects, the impact on defect populations is discussed.

PACS numbers: 61.72.J-, 71.15.Nc, 71.27.+a

Keywords: defect clusters, fluorite structure, nonstoichiometric oxides, uranium dioxide

I. INTRODUCTION

Oxides of the fluorite structure include ZrO$_2$, a common ceramic in research and industry, CeO$_2$, and the actinide oxides ThO$_2$, UO$_2$, and PuO$_2$. The series of actinide dioxides is of great interest in nuclear applications. The present generation of nuclear reactors uses UO$_2$ as nuclear fuel. Fast breeder reactors at present employ mixed (U, Pu)O$_2$, and may in the future use (U, Th)O$_2$. In the oxides of the fluorite or CaF$_2$ structure, MO$_2$, each metal atom M is surrounded by eight equivalent nearest-neighbor O atoms each of which in turn is surrounded by a tetrahedron of four equivalent M atoms. A typical feature of the fluorite structure is the large ($\frac{1}{8}, \frac{1}{8}, \frac{1}{8}$) octahedral holes in which interstitial ions can easily be accommodated. Fluorite structure of UO$_2$ transforms to an orthorhombic Pnma phase under a hydrostatic compression beyond 40 GPa, which in turn followed by an iso-structural transition after 80 GPa. At ambient pressure, however, it exists as the single phase, stoichiometric oxide at all temperature up to 2073 K. Above that it transforms to the sub-stoichiometric phase UO$_{2-x}$, whereas at lower temperatures it easily dissolves large amounts of interstitial oxygen to form anion-excess compositions UO$_{2+x}$. Higher interstitial concentration leads to another ordered phase U$_4$O$_9$, which closely relates to fluorite structure. It was argued that stoichiometric U$_4$O$_9$ does not exist, and should be U$_4$O$_{9-y}$ actually. But for simplicity we still use U$_4$O$_9$ to refer to the non-stoichiometric phase hereinafter. There are three polymorphs of U$_4$O$_9$ between room temperature and 1273 K, known as $\alpha$, $\beta$, $\gamma$, with the $\alpha$/and $\beta$/boundary at 353 K and the $\beta$/boundary at about 873 K. Only the detailed atomic arrangement in $\beta$-phase is clearly determined: the excess anions accommodate in cuboctahedral clusters centered on the 12-fold sites of the cubic space group $I\bar{4}3d$ with the uranium sublattice remains undisturbed. Although the unit cell is 64 times larger than a normal cubic fluorite cell, the average cell is still in fluorite-type except one has to introduce some vacancies at normal anions sites and two types of interstitial oxygen, each sited about 1 Å from the empty octahedral site of the FCC cation sublattice along $\langle 110 \rangle$ (O') and $\langle 111 \rangle$ (O'') direction, respectively. This characteristic is also shared by the $\alpha$-phase and UO$_{2+x}$ with the difference that U$_4$O$_9$ has a long-range ordering for the interstitial oxygen atoms while in UO$_{2+x}$ it is just short-range ordered. To avoid some oxygens too close together, an intuitive proposal that different kinds of oxygen defect are associated to form defect clusters is widely adopted when modeling these
phases.\cite{9,10}

At first sight the fact that interstitials were detected not at the body centers of the cubic interstitial sites but at sites considerably displaced from this symmetric position is puzzling. In rare earth doped alkaline earth fluorides it has conclusively shown that at low interstitial concentrations (1 mole \% or less) the anions occupy the symmetric body center interstitial site, but usually the low-symmetry defect structure is a general feature of anion-excess fluorites.\cite{9,10,11,12,13,14,15,16,17} About half century has elapsed, people still know few about the stabilization mechanism of Willis’ O’ and O’’ sites in energetics. In the limit of \(x \to 0\) in UO\(_{2+x}\), whether the excess-anions will occupy the octahedral interstitial site or not is still unclear. On the other hand, though the occurrence of cuboctahedral clusters in \(\beta\)-U\(_4\)O\(_9\) has been confirmed by experiments, the geometry of defect clusters in low interstitial concentration regime is unknown. One of the simplest model is to assume the Willis 2:2:2 cluster (see Ref.\cite{8} for its geometry) can exist independently and distribute randomly in the material around this concentration. Allen proposed a model for U\(_4\)O\(_9\) in this line by chaining 2:2:2 clusters along \((110)\) direction.\cite{18} Unfortunately his model is definitely wrong because the inconsistencies with experimental facts in: (i) leads to an exact stoichiometric U\(_{4}\)O\(_9\), which might not exist; (ii) no cuboctahedral clusters can be formed in his arrangement; (iii) has an equal concentration for O’ and O’’ sites, against the measurements that O’’ position has a much lower occupancy.\cite{9,10}

Therefore to investigate the geometry and stability of possible defect clusters with a first principles method is required, but it never be easy. The big unit cell of U\(_4\)O\(_9\) and the shortage of information about atomic arrangement in UO\(_{2+x}\) have restricted most of attempts within point defect approximation, and only formation energy of simple intrinsic defects (Frenkel pairs and Schottky defect) were calculated.\cite{11,12,13,14,15,16,17} Applied these energies to point defect model (PDM)\cite{11,12,13,14,15,16,17,18}, however, did not produce satisfactory defect populations — uranium vacancy dominates in the hyperstoichiometric regime, against the experimental anticipation.\cite{11,12,13} The failure might be attributed to the limitation of the PDM which assumes isolated non-interacting point defects, whereas in UO\(_{2+x}\) this is impossible when \(x \geq 0.03\), as we will show later. Also it can arise from the inaccurate energies produced by the local density approximation (LDA) or the generalized gradient approximation (GGA) of the electronic density functional that has been proven failed to describe localized states.\cite{9,10} Nevertheless, some qualitative properties still can access by static calculations within this model. For example the diffusion rate of interstitials can be modeled simply by estimating the migration energy along all possible paths that bridge the initial and final interstitial positions, which is readily computable by ab initio nudged elastic band (NEB) algorithm. For UO\(_{2+x}\), the conclusion is that a direct diffusion is almost prohibited and a normal oxygen on fluorite lattice site must be involved as an intermediate process. That is, the interstitial atom pushes a neighboring lattice oxygen into another interstitial site and itself jumps into the vacancy thus created (interstitialcy mechanism).\cite{19} The extreme of this process is, evidently, creating a transient oxygen dimer, and thus sets up an upper bound to the migration energy for thermodynamical diffusion of oxygens. In order to keep the occurrence probability of oxygen dimer being consistent with experimental observation in bulk U\(_4\)O\(_9\), the energy required to form a such kind of dimer should be much larger than the average migration energy. But this has not yet been confirmed by ab initio calculations. Near to the surface of UO\(_2\) that exposed to air, however, oxygen dimer might become prevailing due to oxidations. And their stability in UO\(_2\) matrix may shed some light on the mechanism of how the material dissolve O\(_2\) molecules into individual interstitials. Also, it serves as to verify the Willis’ assumption that each O’ interstitial has to be associating with one vacancy that occupies the nearest oxygen site;\cite{9,10,11,12,13} since otherwise they must form an oxygen dimer.

These motivate the research work of this paper that mainly focuses on: (i) the stability of isolated point oxygen interstitial in UO\(_{2+x}\) when \(x \to 0\); (ii) the stability and decomposition process of oxygen dimer, including the variations of energy, cell volume and charges, respectively; (iii) the local stability of defect clusters that composed of oxygen vacancies, O’ and O’’ interstitials. These clusters can be viewed as fractal pieces of a cuboctahedral cluster, which is the essential in U\(_4\)O\(_9\) phase. It is believed that the transition from UO\(_{2+x}\) to U\(_4\)O\(_9\) involves long-range ordering of the defect complexes, leading to a change in the symmetry relating the relative positions of the complexes, without producing any atomic re-arrangement within these complexes, i.e., micro-domains of U\(_4\)O\(_9\) should already exist in UO\(_{2+x}\)\cite{9,10,11,12,13,14,15,16,17} What we also want to find out primarily in this paper is what kind of cluster is the most possible candidate for this complex, and its polymorphs when \(x\) is increased. In next section we will brief the calculation method. Main results and discussions are presented in section III. Sec IIIA devotes to formation energy analysis and Sec IIC the charge transfers, in Sec IIIIB and IIIE we will discuss the properties of oxygen dimer in UO\(_2\) and its decomposition process. The defect clustering pattern and its tendency with increased \(x\) are given in Sec IIIF while in Sec IIC a generalization of PDM to include clustering effects is proposed, as well as the associated defect population analysis. Finally in Sec IV we summarize the paper.
II. METHOD OF CALCULATION

Our investigation on defective behavior of UO\textsubscript{2} based on a series of total energy calculations with different configurations in fluorite structure which varied in simulation cell size and defect arrangement. The plane-wave method using density functional theory (DFT) to treat the electronic energy as implemented in VASP code\textsuperscript{22,23} was employed, as well as the projector-augmented wave (PAW) pseudopotentials\textsuperscript{23,24}. The 2s\textsuperscript{2}2p\textsuperscript{3} electrons in oxygen and 6s\textsuperscript{2}6p\textsuperscript{5}f\textsuperscript{6}d\textsuperscript{4}7s\textsuperscript{2} in uranium were treated in valence space. The cutoff for kinetic energy of plane waves was set as high as 500 eV to eliminate the possible Pulay stress erroneous. Also it has been elevated due to the presence of oxygen which requires an energy cutoff at least 400 eV to converge the electronic energy within a few meV. Integrations over reciprocal space were performed in the irreducible Brillouin zone with about 8–36 non-equivalent k-points, depending on the system size. The energy tolerance for charge self-consistency convergence was set to $1 \times 10^{-5}$ eV for all calculations. And the total convergence of this parameter set was checked well. Without a specific statement, all structures in following discussions have been fully relaxed to get all Hellman-Feynman forces (stress) less than 0.01 eV/Å.

The electronic exchange-correlation energy was computed by spin-polarized local density approximation with an effective on-site Coulomb interaction to split the partially filled 5f bands localized on uranium atoms (LSDA+U)\textsuperscript{22,23}. Parameters of the Hubbard term were taken as $U = 4.5$ eV and $J = 0.51$ eV, which has been checked carefully for fluorite UO\textsubscript{2}\textsuperscript{22-25,26}. Here some comments are desired. It is well known that it is the $U$ but $J$ that contributes to electronic structure sensitively. In UO\textsubscript{2} case, the value of $U$ quite depends on the atomic arrangement of uranium atoms. If uranium sublattice almost being unchanged, as the case here concerned, one can expect the $U$ would not vary too much. On the other hand, the influence of interstitial oxygens on localized 5f electrons should be small if they are well separated from uranium atoms. However, as interstitial concentration increased, the impact on $U$ may become non-negligible. Therefore we must restrict to certain composition regime, and $x \leq 0.25$ should be small enough to allow using this set of parameters. This composition value can be estimated roughly by checking the induced deformation on the uranium sublattice. The situation of uranium defects is a little embarrassed. We cannot estimate its effect on $U$ until a more accurate functional becomes generally available, for example, the hybrid density functional that has shown impressive versatility in preliminary applications\textsuperscript{22}. However, for a point defect in a large enough cell, to neglect this influence seems reasonable. Another point is about the adoption of LSDA+U functional instead of GGA+U. The latter has been proven as of a poor description to the defect energetics, which we will discuss in details in Sec III C.

The supercell method has been used to model defect structures. Periodic boundary conditions were imposed on the whole system. The geometry of all structures (except those in Sec III F) are listed in table I, where each brick indicates a fluorite cubic unit cell (in U\textsubscript{4}O\textsubscript{8}), and red points represent oxygen interstitials, which usually occupy the cubic centers, except those associated with dimers. Dot-lined box (if drawn) indicates the oxygen cage. No atom on the fluorite lattice has been drawn explicitly, except in C\textsubscript{4}d\textsubscript{1} and C\textsubscript{4}d\textsubscript{11} where the lattice oxygens bonded to interstitials were also plotted. Each structure of C\textsubscript{4}d\textsubscript{1}, C\textsubscript{4}d\textsubscript{2} and C\textsubscript{4}d\textsubscript{11} contains one oxygen dimer, respectively. Configuration "C8\textsubscript{1}" has the same geometry as C\textsubscript{8} but replacing the interstitial oxygen with one uranium, and "C8\textsubscript{−1}" or C\textsubscript{8} corresponds to remove one lattice atom from a system with 8 fluorite cubic cells (2 × 2 × 2).

The magnetic effects have been taken into account by initially set up an antiferromagnetic orientation of atomic moments. Two cases, the moment ordering along the longest (L) and shortest (S) axis, are considered. The cohesive energy $E\textsubscript{coh}$ of each structure is calculated from the total energy by subtracting the isolated spin-polarized atomic contributions. Then the oxygen defect formation energy in structure $Cm\textsubscript{n}$ is given by

$$E_f = E\textsubscript{coh} - mE\textsubscript{coh}^1 - \frac{n}{2} E\textsubscript{O2}.$$  

(1)

Here $m$ is the number of fluorite cubic cells and $n$ the total oxygen interstitials or vacancies. $E\textsubscript{O2}$ is the binding energy of a neutral dioxygen molecule. Alternatively, one can define an alloy-system like formation energy by choosing $C1$ as one of the reference phases instead of $O$ molecule. We call it the relative formation energy, which takes the advantage of showing the phase stability of superstructures with different composition explicitly, analogous to that in an alloy and compound system\textsuperscript{28,29}. It thus can be calculated as

$$E_{Rf} = E\textsubscript{coh} - (1 - \frac{n}{m})E\textsubscript{coh}^1 - \frac{n}{m} E\textsubscript{coh}^1,$$

(2)

and the value of $n/m$ stands for the composition of phase $C1$ in $C1$, or equivalently, the concentration of oxygen interstitial per fluorite cubic cell. All configurations incorporated with uranium defect are marked by a superscript $\alpha$ in table II and the formation energy for a defect in $\alpha Cm\textsubscript{n}$ is defined as

$$E_f = E\textsubscript{coh} - mE\textsubscript{coh}^1 - nE\alpha.$$

(3)

Here $E\alpha$ is the cohesive energy per atom in the metallic $\alpha-U$ phase, and we use the experimental value of $−5.4$ eV for simplicity\textsuperscript{30}.
TABLE I: Equilibrium properties of uranium dioxide with defects: superscript $u$ denotes uranium defects and negative subscript refers to vacancy. $\Delta V$ is the volume difference relative to $C1$ structure and $E_f$ the defect formation energy per point defect. Note $E_{coh}$ and volume have been averaged to a single fluorite cubic cell.

| Label  | $E_{coh}$(eV/cell) | Volume($\text{Å}^3$/cell) | $\Delta V$($\text{Å}^3$/cell) | $E_f$(eV) | Structure |
|--------|--------------------|-----------------------------|-------------------------------|-----------|-----------|
| $C1$   | -98.638            | 161.34                      | 0.0                           | 0.0       | ![Image]   |
| $C1_1$ | -102.906           | 157.17                      | -4.17                         | -1.394    | ![Image]   |
| $C2_{1}(L/S)$ | -101.20/-101.199 | 159.47/159.46              | -1.87/-1.88                   | -2.249/-2.248 | ![Image] |
| $C4_{1}(L/S)$ | -99.71/-99.731 | 160.54/160.28              | -0.8/-1.06                    | -1.413/-1.496 | ![Image] |
| $C4_{1d}(S)$ | -99.337           | 162.87                      | 1.53                          | 0.079     | ![Image]   |
| $C4_{2d}(S)$ | -100.486          | 163.05                      | 1.71                          | -1.642$^a$ | ![Image]   |
| $C4_{1d1}(S)$ | -100.461          | 162.09                      | 0.75                          | -1.545$^a$ | ![Image]   |
| $C4_{2}(L/S)$ | -101.233/-101.237 | 159.35/159.38              | -1.99/-1.96                   | -2.316/-2.324 | ![Image] |
| $C8_{1}$ | -99.268            | 161.05                      | -0.29                         | -2.169    | ![Image]   |
| $C3_{1}^{L}$ (L/S) | -100.099/-100.361 | 160.25/160.16              | -1.09/-1.18                   | -1.509/-2.294 | ![Image] |
| $C3_{2}^{L}$ (L/S) | -101.789/-101.788 | 159.34/159.36              | -2.0/-1.98                    | -1.853/-1.850 | ![Image] |
| $^{a}C8_{1}$  | -97.338            | 161.54                      | 0.20                          | 7.525     | -         |
| $^{a}C8_{1}$  | -98.289            | 164.25                      | 2.91                          | 8.194     | -         |
| $^{a}C8_{-1}$ | -96.831            | 160.26                      | -1.08                         | 9.056     | -         |

$^a$ per two oxygen interstitials

Vibrational frequencies of interstitial oxygens were calculated by finite difference method with frozen phonon approximation. At finite temperatures, these vibrational frequencies contribute to the first order of defect free energy directly, which is given by $F(T) = E_f - \kappa_B T \ln Z_v$, with the partition function

$$Z_v = \prod_i \sum_{j=0}^{\infty} \exp \left( \frac{-E_j^i}{\kappa_B T} \right),$$

where $\kappa_B$ is the Boltzmann constant and $E_j^i$ the eigenvalue energy for the $j$-th vibrational mode with frequency $\omega_j$, and the harmonic approximation $E_j^i = \hbar \omega_j(j + \frac{1}{2})$ has been used. Mind here we have not subtracted the vibrational free energy of the reference state $O_2$ molecule, and comparison of the calculated free energies therefore can be made only among configurations with the same number of interstitial oxygens.

Regarding charge transfer calculations, it is well known that the concept of static atomic charge in ab initio calculations usually leads to ambiguity due to the arbitrariness in determining the belongingness of electrons. Nevertheless, there are several methods exist to compute the effective atomic charge, which do provide some useful qualitative understanding. Among those the Bader’s conception that to partition an electronic density by surfaces formed by the density minimums (zero flux surfaces) is one of the most intuitive. It is simple to calculate Bader charges, requiring only atomic positions and electronic density as input. The partition surfaces are determined by finding the charge density minimums. Then the atomic charge is obtained by subtracting the valent electrons from the integral of charge density over the space surrounded by the partition surfaces that envelops the atom. Another widely used
concept is dynamical effective charge, defined by the change of polarization induced by atomic displacements, which is beyond the scope of this paper and will not elaborate here.

III. RESULTS AND DISCUSSIONS

A. Dioxygen molecule

We first discuss the dioxygen molecule. The O\(_2\) molecule was modeled by putting it in a periodic cubic cell with a lattice constant of 15 Å, large enough to eliminate the factitious interaction among its images. Only one k point (\(\Gamma\)) was used. Since the notorious failure of LDA in description small isolated molecules, we employed here (and only here) the revised Perdew-Burke-Ernzerhof (\(\text{rPBE}\)) GGA electronic exchange-correlation functional. The bond length was optimized to be 1.22 Å, in a good agreement with experimental 1.21 Å. The calculated binding energy is \(-5.75\) eV, a little deeper than observed \(-5.1\) eV. This discrepancy should attribute to the difficulty of current functional to take into account the van der Waals interactions accurately. The vibrational frequency of stretch mode, however, was well reproduced as 1588.6 cm\(^{-1}\), against the experimental 1580.2 cm\(^{-1}\). As a check to the validity of Bader’s conception, we calculated the Bader atomic charge for each oxygen atom in O\(_2\) and got them as \(\pm 0.09\) e, reflects the essential of covalent bond correctly. The deviation can be reduced further when in an ionic bond environment where the charge density minimum surfaces sharply show up.

B. Structure and formation energies

1. Oxygen interstitials

The calculated equilibrium properties of 14 configurations, including cohesive energies, equilibrium volumes, volume changes relative to the ideal UO\(_2\) cell and defect formation energies are listed in table I. These data have been averaged to one fluorite cubic cell. It can be seen that the cohesive energy always decreases as oxygen interstitial concentration increased, demonstrating the tendency of uranium dioxide to dissolve oxygens. The solubility, however, cannot be determined by simply taking the limit of this cohesive energy vs concentration curve. Also, the relative stability among different configurations has been obscured here. To get that information explicitly, one needs back to the relative formation energy.

One interesting thing is that we find except that of oxygen dimer, introducing point oxygen interstitials always shrinks the system, \(i.e.,\) leads to a negative \(\Delta V\), as shown in figure I. This feature differs from GGA results, which...
but agrees with GGA+U\textsuperscript{37} and may attribute to the behavior of localized 5f electrons. Generally, a negative $\Delta V$ means the interaction between the matrix and the interstitials is dominated by attractive chemical potentials rather than by mechanical effects (atomic size effect). The latter always results in a swollen volume and is important for big interstitial atoms or inert gases. Oxygen dimer belongs to this class and requires extra space to accommodate, which can be seen more clearly when compare an isolated defect approximation and other configurations must be interpreted as ordered defect phases.

C\textsuperscript{2+} which can be understood in terms of thermal vibration effects and extensive energetics of perfect bulk UO\textsubscript{2+x} \textsuperscript{13} and may attribute to the behavior of localized 5f states. Generally, a negative $\Delta V$ means the interaction between the matrix and the interstitials is dominated by attractive chemical potentials rather than by mechanical effects (atomic size effect). The latter always results in a swollen volume and is important for big interstitial atoms or inert gases. Oxygen dimer belongs to this class and requires extra space to accommodate, which can be seen more clearly when compare C\textsubscript{41d} with C\textsubscript{41} and C\textsubscript{41d1} configurations. The influence of magnetic orientation on equilibrium volume is almost negligible except in the cases of C\textsubscript{41} and C\textsubscript{3f}, of which only C\textsubscript{3f} has a notable formation energy difference between L and S orientation.

The calculated slope of volume variation induced by oxygen interstitials (the solid line in figure 1) is in a good agreement with experimental change of the lattice constant $a \approx 5.4696 - 0.1495x$ as reported by Alekseyev et al. for homogenous UO\textsubscript{2+x} powders as quoted in Ref.\textsuperscript{28} (the dashed line). Also, it is in accord with the volume change of $\beta$-U\textsubscript{4}O\textsubscript{9} measured at room temperature\textsuperscript{12} with respect to that of stoichiometric UO\textsubscript{2}.\textsuperscript{1} Increase temperature to 503 K and 773 K expands the material greatly\textsuperscript{5} which can be understood in terms of thermal vibration effects and extensive defects generation.

Figure 2 shows the defect formation energies of oxygen interstitial in all considered configurations of UO\textsubscript{2+x} within 0 $\leq x \leq$ 0.25. Note the value of C\textsubscript{42d} and C\textsubscript{41d} are for two interstitials. A remarkable feature in this graph is that in energetics an oxygen dimer mimics a single oxygen atom. Comparing that of the perfect crystal C1 with C\textsubscript{41d}, and that of C\textsubscript{41} with C\textsubscript{42d} and C\textsubscript{41d1}, we see that despite the latter contains one more interstitial, the formation energy is almost the same. That means to absorb an oxygen from O\textsubscript{2} gas into UO\textsubscript{2} and forms a dimer will neither release nor gain heat. Point interstitial and dimer would have almost the same behavior except that a dimer needs a bigger space for accommodation. This mimic is also supported by Bader effective charge calculations: they have almost the same charge too (see below). However, this does not suggest the stability of oxygen dimers in UO\textsubscript{2} since point oxygen interstitial always has a lower per atom formation energy.

Our calculations also present a remarkable system size dependence in formation energy, contrasts to that of GGA results where a value of $-2.6$ and $-2.5$ eV were obtained for C\textsubscript{1} and C\textsubscript{2} configurations (almost size-independent), respectively,\textsuperscript{28} revealing the limitation of applying the pure GGA to defects in spite of its impressive performance in energetics of perfect bulk UO\textsubscript{2}.\textsuperscript{2} No magnetic ordering and volume relaxation were considered in that GGA calculation.\textsuperscript{28} A discrepancy about 1.2 eV with our result for C\textsubscript{1}, however, cannot be covered by these effects since volume relaxation would definitely increase the discrepancy and magnetic contribution can not be of that magnitude, and it therefore should attribute to the behavior of localized 5f states.

The deepest formation energy shown in figure 2 is $-2.32$ eV (configuration C\textsubscript{42}), rather than the isolated approximation of a point interstitial’s (C\textsubscript{81}) $-2.17$ eV. Actually, except those configurations with 8 fluorite cubic cells, the defects in all other structures cannot be interpreted as isolated ones because the non-negligible interactions among their images arisen from periodic conditions. This invalidates the defect stability analysis based on their formation energy directly. Mapping these configurations onto an alloy system can circumvent this difficulty. Namely, to view these configurations (discard those with dimer) as an alloy system with oxygen interstitials distributing over the fluorite cubic centers (U\textsubscript{4}O\textsubscript{8+y}). Then the extreme phases of this system are C\textsubscript{1} and C\textsubscript{11}. Following this way, figure
transforms into figure 3 with the help of Eq. (2), where the solid line indicates the ground state hull. We then find that $C3^L_1(S)$ and $C3^L_2$ are close to be ground states, while $C8_1$, the isolated point interstitial approximation, will decompose into a mixture of $C1$ and $C4_2$ phases. That means, defect clustering is inevitable when $x \geq 0.03$. Since $C4_2$ may not be the physical ground state (mind neutron diffraction experiments suggested that no octahedral site should be occupied around this composition), this limit can be lowered further. On the other hand, it seems reasonable to assume that $C8_1$ has already approached the limit of an isolated point interstitial, namely, no notable formation energy would be gained or lost if enlarge the system to $C27_1$ or $C64_1$. If it is true, then the isolated point interstitial will always exist when $x \to 0$. Its site, according to structure symmetry, should be the octahedral position. It is worthy to note that the PDM fails at about $x \sim 10^{-3}$ instead of $10^{-2}$ with GGA formation energies. This two orders discrepancy is owing to the inaccuracy of the formation energies they used, which can be improved greatly by LSDA+U method, see Sec.III G for details.

2. Other defects

Point oxygen vacancy and uranium defects are all modeled in a system with 8 fluorite cubic cells. Namely by $C8_{-1}$ and $u C8_{\pm 1}$. The volume change in $C8_{-1}$ is in accord with that of point oxygen interstitials: linearly decreasing with an increased $x$, fitting to $\Delta V = 0.01 - 14.7x$, as shown by the solid line in figure 1. Uranium vacancy also obeys this law, whereas the interstitial has a much rapid change. Totally, they still decrease monotonically with $x$, but no longer in linear. All three defects have a formation energy larger than 7 eV, in contrast to previous ab initio results. We prefer to postpone this discussion to Sec.III G with Frenkel and Schottky defects together.

C. Charge transfers

It has long been believed that dissolve oxygen in UO$_2$ will oxidize U$^{4+}$ to U$^{5+}$, even U$^{6+}$ state. The exact charge transfer induced by defects, however, is unclear. Qualitative analysis is accessible to this problem with empirical shell model, nevertheless the calculated energy depends on atomic positions sensitively, obscuring its applicability to defects with noticeable structure deformations. A direct calculation of the charge state from first principles is therefore desired.

1. Oxygen interstitials

The calculated Bader effective charges using electronic density generated with VASP code are listed in table II, where the interstitials and the lattice oxygens that forming a dimer are excluded from the average operations, and
### TABLE II: Bader effective charges of UO$_2$ with defects: average charge $q$, standard deviation $\sigma$, difference from that in perfect UO$_2$ $\delta q$ and the maximal transferred charge $\Delta_{\text{max}}$ ($\pm 0.02$). All in the unit of positron charge $e$.

| Label | defects | uranium | oxygen |
|-------|---------|---------|--------|
|        | $q$     | $\sigma$ | $\delta q$ | $\Delta_{\text{max}}$ | $q$     | $\sigma$ | $\delta q$ | $\Delta_{\text{max}}$ |
| C1     | –       | 2.56    | 0.0     | 0.0     | -1.28   | 0.0     | 0.0     | 0.0     |
| C1$_1$ | -1.04   | 2.62    | 0.11    | 0.07    | 0.26    | -1.18   | 0.004   | 0.10    | 0.11    |
| C2$_1$(L/S) | -1.15   | 2.63    | 0.11    | 0.08    | 0.27    | -1.24   | 0.02    | 0.03    | 0.07    |
| C4$_1$(L/S) | -1.18/-1.14 | 2.60    | 0.08    | 0.04    | 0.25    | -1.26   | 0.03    | 0.02    | 0.08    |
| C4$_{1d}$(S) | -0.61(-0.77) | 2.56    | 0.02    | 0.01    | -0.03   | -1.28   | 0.01    | 0.0     | -0.03   |
| C4$_{2d}$(S) | -0.66,-0.59 | 2.60    | 0.08    | 0.04    | 0.26    | -1.26   | 0.03    | 0.02    | 0.12    |
| C4$_2$(L/S) | -1.19/-1.20 | 2.61/2.63 | 0.10    | 0.07    | 0.23/0.25 | -1.24   | 0.02    | 0.04    | 0.07    |
| C8$_1$ | -1.24   | 2.58    | 0.05    | 0.03    | 0.24    | -1.27   | 0.02    | 0.01    | 0.05    |
| C3$_{1d}^4$(L/S) | -1.16   | 2.60    | 0.09    | 0.04    | 0.25    | -1.25   | 0.03    | 0.03    | 0.10/0.08 |
| C3$_{2d}^4$(L/S) | -1.10,-1.13 | 2.64    | 0.11    | 0.09    | 0.26/0.28 | -1.23   | 0.02    | 0.05    | 0.09    |
| $\text{aC8}_1$ | 1.61    | 2.51    | 0.09    | -0.04   | -0.25   | -1.28   | 0.01    | -0.00   | -0.03   |
| $\text{aC8}_1$ | –       | 2.59    | 0.08    | 0.04    | 0.26    | -1.26   | 0.03    | 0.02    | 0.13    |

$a$ value in parenthesis is for the atom sited on oxygen sublattice.

list of the electronic properties of uranium and oxygen that were used in the calculation of the charge state close to the lattice oxygens, especially in the case of uranium atoms, except two of them lost about 0.24 e$^{-2}$ directly. Considering oxygen and uranium in perfect UO$_2$ have only a charge of $\sim 1.28$ and $2.56$ e$^{-2}$, all are smaller than the nominal chemical valences but close to that of a partially ionic model that widely used in semi-empirical potentials.\cite{41,42} we can re-interpret the Bader charges by multiplying a scaling factor to make them comparable with the chemical valences. In this sense the change of the charge state in these two uraniums should be about 0.5 e$^{-1}$, i.e., they are oxidized to U$^{4.5+}$ instead of U$^{5+}$. The transferred charges, however, cannot cover the amount absorbed by the interstitial oxygen, and all other normal uraniums and oxygens have also lost a small portion of their charge. This observation contrasts to the conventional expectation and reveals the difficulty to oxidize uranium to a higher valence state. The charge transfer in other configurations also support this point: in all cases each oxygen interstitial can oxidize two and only two uraniums to U$^{4.5+}$ while leaving others almost unchanged, no higher valence state of uranium has been observed. As to which uranium is apt to be oxidized, obviously the answer is the nearest neighbors (NN) of the defect, but oxidation of some next NNs also was observed. It is worthwhile to point out that we did not find a sensitive dependence of the charge state on Hubbard $U$ parameter.

The more deformed the geometry is, or equivalently, the more interstitials the system contains, the charge state of lattice atoms are disturbed more drastically. It is clear by comparing the charge transfer in C$3_{1d}^4$ with C$3_{2d}^4$, or C4$_1$ with C4$_2$. The largest $\Delta_{\text{max}}$ for oxygen takes place in C1$_1$ with the largest composition, and in C4$_{2d}$ with a dimer. The smallest $\Delta_{\text{max}}$ for uranium and oxygen are in C4$_{1d}$, also containing a dimer, both are $\sim 0.03$ e$^{-1}$. The difference between C4$_{1d}$ and C4$_{2d}$ is the former contains only one interstitial which bonds to a lattice oxygen and the latter contains two interstitials that bonding to each other. Table III illustrates that in the former case no charge has been transferred from other lattice atoms, and only charge redistribution within the dimer is involved that making it has a total charge close to a lattice oxygen; in the latter case, however, absorbing charges from other atoms is necessary and gives them a similar charge state as the interstitial in C4$_1$, especially only two uraniums are oxidized to U$^{4.5+}$ state here in spite of there are two interstitials presented. The total charge of the dimer, $\sim 1.25$ e$^{-1}$, close to a lattice oxygen in UO$_2$, indicates it should be O$_2^{2-}$ actually.

It is worthwhile to note that oxygen changes its charge state almost continuously but it is discrete for uranium when lost its charge. That is, except those atoms who lost $\sim 0.25$ e$^{-1}$, the changes of charge in other uraniums are less than 0.03 e$^{-1}$. Moreover the discrete lose of charge is always accompanied by lowering the local moment of uranium from $\sim 2\mu_B$ to $\sim 1\mu_B$. Since the local moment of uranium in UO$_2$ originates from localized 5f states, it is obvious that 5f electrons contribute to this process greatly. This can be understood in the partially ionic charge model: although the chemical valence of uranium in UO$_2$ is 4+, table III shows in fact the physical valence has only 2.56+. Namely, only the 7s$^2$ and a fraction of 6d$^1$ electrons are completely transferred to oxygen. Uranium cation still holds about 0.24 e$^{-1}$ of the 6d$^1$ electron and other remainder forms two weak U-O covalent bonds, each has a portion of $\sim 0.2$ e$^{-1}$. When
oxidized by oxygen interstitials, the cation loses its 6d electron completely (transferred to the interstitial atoms). As a consequence one of the localized 5f states becomes the outermost orbit, which spreads extensively and eventually the cation lost half of its local moment. This mechanism also explains the difficulty to oxidize uranium to a higher charge state since transferring a 5f electron requires much larger energy than 6d one.

2. Other defects

In point oxygen vacancy case (configuration $C8_{−1}$), the uranium cations gain charges and decrease the average valence to 2.53+, but the disturbance to remain oxygen is small. The largest charge transfer for uranium is $−0.34\,e$, associating with three other uranium atoms each of them gets an extra charge about $−0.25\,e$, respectively. Compared with the interstitial case, here no notable change in local moment was observed. The value of $−0.34\,e$ implies the cation has retracted the portion of electrons shared by the removed oxygen ($∼0.1\,e$), and the $−0.25\,e$ indicates that each quarter-filled states of 6d electrons seems stabler than continuous occupancy.

Point uranium vacancy is analogous to two oxygen interstitials in that there are four uranium cations lost the charge, three NNs and one next next NN, ranging from 0.23 to 0.26$\,e$. All of them also lost half of their local moments. The change in other uraniums is negligible. However, it disturbs the oxygens severely, with a $\Delta_{max}$ as high as 0.13$\,e$, even though the averaged charge is still close to the perfect one. The oxygen charge state in $^{238}\text{C8}_1$ is almost the same as in $C8_{−1}$, except that here there are six (NNs) instead four uraniums gain charge, ranging from $−0.19 ∼ −0.25\,e$. Again, no apparent impact on other atoms. The extra charge provided by the interstitial uranium is almost absorbed by its six NNs completely. The magnetic ordering has been damaged severely, and the change in exchange interaction has made some 5f electrons flip their spins, but no uranium was observed to have a moment of $∼1\,\mu_B$.

D. Oxygen dimer in UO$_2$

As previous sections mentioned, although oxygen dimer has a similar behavior in energetics and charge state as a single oxygen interstitial, it actually is an ionic molecule, and formed when oxygens are forced to close to each other enough. But this is difficult due to the energy barrier between the individual atoms. In UO$_2$, irradiation provides enough excess energy to overcome this barrier. For example in an $\alpha$ decay the recoil of the daughter nucleus produces a ballistic shock with an energy release of about 70 keV,$^{33,34}$ which frequently takes place in nuclear fuels. Nonetheless this cannot survive the dimers to equilibrium conditions, even if they do appear transiently. Another situation where oxygen dimers can be observed is near the surfaces exposed to oxygen gas. Oxygen molecules adsorbed onto the UO$_2$ surface will obtain additional charges then diffuse inwards. Decomposing the molecule at the vacuum side of the surface is almost impossible due to the large binding energy, while in UO$_2$ side it prefers to oxygen sublattice
sites instead of the interstitial positions, where it decomposes into individual interstitials, with a barrier only about 0.21 eV (see below).

Figure 4 shows the difference charge density (reference to the corresponding atomic charge) of an oxygen dimer in UO$_2$ ($C4_{2d}$) projected to [100] plane, as the arrow indicates. The covalent bond between two interstitial oxygens presents evidently. A similar picture has been observed in $C4_{1d}$ configuration or a natural O$_2$ molecule. Analysis shows that it in fact is an O$_2^{2-}$, with the two additional electrons occupying the 2$p\pi^*$ antibonding orbitals and the final bond order is one. The calculated bond length is 1.39Å, slightly short than experimental 1.49Å. This discrepancy owes to the compression from oxygen cage and can be removed. For example when the dimer is formed by bonding to one lattice oxygen ($C4_{1d}$), where although the charge state is still similar ($-1.38\, e$), the bond length extends to 1.47Å, in a good agreement with experimental data.

Accommodation oxygen dimer in UO$_2$ leads to a swollen of the system volume (see table I). The induced stress forces them orientated in ⟨111⟩ direction and occupy the Willis O$^\prime\prime$ sites actually. In energetics, oxygen dimer in UO$_2$ is meta-stable, see figure 2. Its decomposition process can be modeled by successively moving the interstitial oxygen (as a test atom) in $C4_{1d}$ along the ⟨111⟩ direction till to the cubic center, which is the most possible separate path. The resulted potential shape is shown in figure 5 where $\delta d$ is the initial depart distance between the two oxygens and $\Delta d$ the final (dimer) length. The structure frozen line was obtained by fixing the cell and all other atomic positions whereas the optimized one resulted from a fully relaxation of the cell volume and shape and the nearby atomic coordinates that surrounding the defect.

Note a distance of $\delta d = 2.2\, \text{Å}$ stands for the state that the initial position of the test oxygen already close to the cubic center. From figure 5 we get the critical distance to break a dimer is about 1.73Å, with a barrier of 0.21 eV. Inset gives the variations of system volume and Bader atomic charges of the two oxygens, demonstrating a drastic behavior around the breaking point. Two points need to be noticed here: the large charge transfers and the contraction of system volume. The later confirms that atomic size effect is not an important factor for oxygen interstitials in UO$_2$ where chemical interaction overwhelming. A deduction of this is that a single oxygen interstitial can occupy a site other than the cubic center, regardless it has the largest space. Indeed, no experiment has detected the occupation of this site in UO$_{2+x}$ when $x \geq 0.1$. Chemical interaction might prefer other sites if volume is expanded. As the “structure frozen” line shows, interstitial oxygen is apt to forming dimers when the volume is fixed at 651.49 Å$^3$. Therefore, oxygen dimers may also exist at regions with negative stresses.

As the limit case of an interstitialcy diffusion model, to form an oxygen dimer in UO$_2$ requires an energy of $\sim 1.75\, \text{eV}$ (figure 5), compatible with the NEB migration energy of 1.11 eV. This magnitude of migration energy corresponds to $\delta d \approx 1.8\, \text{Å}$, with an equilibrium intra-atomic distance about 2.0 Å and the atomic charges $\sim -1.0\, e$. Therefore a charge oscillation induced by oxygen diffusion is about 0.2 e, almost the same level as to oxidize one uranium.
TABLE III: First principles results for structural, energetic, and vibrational properties of oxygen interstitial and O\textsubscript{2} dimer in different configurations. For comparison, calculated values for O\textsubscript{2} in vacuum are also listed. Δ\textit{E} is the energy difference between interstitial O/O\textsubscript{2} and vacuum O\textsubscript{2} (formation energy per pair interstitials), \(d_0\) is the equilibrium bond length, \(q\) is the Bader effective charge, \(\omega\) is the harmonic frequency. Note the \(q\) in the last row is just for to label the experimental conditions.

| Label | \(\Delta E\) (eV) | \(d_0\) (Å) | \(q\) (e) | \(\omega\) (cm\textsuperscript{-1}) |
|-------|-----------------|-------------|----------|-----------------|
| C\textsubscript{21} | -4.496 | - | -1.15 | 292.5, 316.7, 403.9 |
| C\textsubscript{41} | -2.993 | - | -1.14 | 373.3, 386.6, 397.5 |
| C\textsubscript{41d} | 0.159 | 1.47 | -0.61(-0.77) | 273.6, 345.3, 353.9 |
| C\textsubscript{42d} | -1.642 | 1.39 | -0.66,-0.59 | 447.4, 482.3, 496.6 |
| Vacuum | 0 | 1.22 | | 608.5, 637.2, 995.4 |
| Expt. | - | 1.21/1.49\textsuperscript{a} | 0.0/-2.0 | 1588.6 |

\textsuperscript{a} Ref. \[32\] \textsuperscript{b} Ref. \[34\]

E. Vibrational frequencies

Raman and infrared spectroscopies provide information about atomic vibrations. These techniques can be employed to detect defect clusters by searching the characteristic vibrational frequencies. At finite temperatures, these frequencies directly contribute to the formation energy and structural thermodynamic stability.

Vibrational frequencies of single oxygen interstitial (has three modes) and dimer (has six modes) in C\textsubscript{21}, C\textsubscript{41}, C\textsubscript{41d} and C\textsubscript{42d} configurations were calculated. In all calculations, we aligned the magnetic ordering direction along the shortest axis (S), which always has the lowest energy. Only harmonic frequencies were computed here and has omitted all anharmonic effects. For fluorite UO\textsubscript{2}, we have checked that the contribution from the latter is very small for oxygen and uranium interstitials (within ±3 cm\textsuperscript{-1}). Table III lists the calculated frequencies (\(\omega\)), as well as the equilibrium bond length for dimers (\(d_0\)) and formation energies (\(\Delta E\)). Due to the compression from oxygen cage, the vibrational frequencies in C\textsubscript{42d} have greater value than their counterparts in C\textsubscript{41d}. The stretch model of O\textsubscript{2} molecule (with the largest \(\omega\)) has been greatly softened when incorporated in UO\textsubscript{2}. This is analogous to the incorporation of H\textsubscript{2} in an interstitial position of semiconductors\textsuperscript{46} where a decrease of the binding energy, an increase in the bond length, and a lowering of the vibrational frequency was observed. The underlying physics, however, might be different. In this case, by comparing the calculated Bader effective charges with the partially ionic model of UO\textsubscript{2}\textsuperscript{2+} we can identify the nominal charge of the oxygen dimers should be about −2.0 e. The variation of bond length confirms this interpretation. Consequently, the frequency of stretch model is lowered from 1588.6 cm\textsuperscript{-1} to 995.4 cm\textsuperscript{-1} in C\textsubscript{42d} and 795.4 cm\textsuperscript{-1} in C\textsubscript{41d}.

According to the calculated static energies, C\textsubscript{42d} will decay to C\textsubscript{21}, and C\textsubscript{41d} to C\textsubscript{41} eventually (see \(\Delta E\) in table III). Computed frequencies indicate thermal vibrations would accelerate this process further. Figure IV gives the differences of free energy between C\textsubscript{42d} (\(\Gamma_d\)), C\textsubscript{21} (\(\Gamma_s\)), C\textsubscript{41d} (\(\phi_d\)) and C\textsubscript{41} (\(\phi_s\)) calculated with their formation energies (table I) and vibrational frequencies (table III), respectively. The rapid drop of the free energy differences with increased temperature implies that meta-stable oxygen dimers in UO\textsubscript{2} have a very short lifetime at finite temperatures, and with little possibility to occupy the cubic center sites: they must have been decomposed before enter the oxygen cage.

F. Defect clustering in UO\textsubscript{2+x}

This section devotes to the possible defect clustering pattern in UO\textsubscript{2+x}. Instead of compute the formation energies directly, we focus on the local stability of O\textsuperscript{−} and O\textsuperscript{2−} sites in different circumstances here. This method cannot determine what cluster is the most stable one, but it does rule out some combinations of O\textsuperscript{−}, O\textsuperscript{2−} and oxygen vacancies.

For this purpose we calculated the potential landscape felt by a test oxygen atom. Just one fluorite cubic unit cell was used. Here since the cell and all atomic coordinates have been frozen up except that of the test oxygen, the error introduced by periodic conditions is proportion to the second order of the charge density variation \(\delta\rho\) that induced by images of the test atom. This precision is enough for a qualitative analysis (Mind ionic interactions among the test atom’s images contribute only a constant to the energy and therefore irrelevant to the problem).
FIG. 6: Variation of free energy difference contributed from interstitial vibrations. Inset: the free energies of a dimer in C42d and its relative stable state C21 as a function of temperatures.

FIG. 7: (Color online) Potentials for an oxygen interstitial in UO2 along ⟨111⟩ (left) and ⟨110⟩ (right) direction crossing the cubic center. The numerics refer to lattice constant and arrows point to the position of O′ or O′′ site. Fractional coordinate 0.5 denotes the cubic center.

1. Local stability of basic clustering modes

At first we check the local stability of a single O′ and O′′ site. Figure 7 shows the potential shapes crossing these two sites. It is seen that O′′ site becomes meta-stable when the lattice constant increases to about \( a = 5.44 \) Å. And isotropic expansion stabilizes this site further which makes it the global minimum if \( a \geq 5.6 \) Å. A single O′′ interstitial actually forms a dimer with the nearest lattice oxygen and this behavior is in consistence with the structure frozen curve in figure 5. However, this effect does not benefit the stabilization of O′ site. Under ambient conditions the experimental lattice constant for UO2+x is within 5.45 ∼ 5.47 Å, therefore a single O′ or O′′ oxygen interstitial (as well as clusters formed by them only) is almost unstable.

The simplest cluster involved one oxygen vacancy, say a V-O′ or V-O′′ pair, is obviously unstable since nothing can prevent them from annihilation. The next triple cluster is V-O′ (O′′) pair stabilized by an O′ or O′′ interstitial. Considering the short distance between the nearest O′ and O′′ sites, the situation should be quite similar for them.
Therefore hereinafter we only consider the cases that incorporated with V-O' pairs. The potential shape for an O'(O'')-V-O' cluster was calculated in an analogous manner except a lattice oxygen (0.75,0.75,0.75) was moved to (0.883,0.5,0.883), a nearest O' site, to create the V-O' pair, as shown in figure 8. Although the curve along ⟨110⟩ already changes asymmetrically about the cubic center (with a fractional coordinate 0.5), O' is locally unstable since it will decay to O'' (with a swallow trap) then finally to a position beyond the (0.75,0.75,0.75) site. This rules out the O'-V-O' (V-2O') and O''-V-O'' (V-2O'') triple clusters that distribute symmetrically about a lateral of the oxygen cage.

To stabilize the O' site locally, we have tried all possible combinations and find two nearest oxygen vacancies seems necessary. Figure 9 gives the potentials that incorporated with two V-O' pairs. Mind these O' sites should be in otherwise empty oxygen cubes that do not share the lateral linking the two vacancies with the original one. The pairs are thus created by moving (0.75,0.75,0.75) oxygen to (0.617,1.0,0.883) and (0.75,0.75,0.25) to (1.0,0.617,0.117), respectively. We see it do prefer the O' but not O'' site. In fact this cluster would become the Willis 1:2:2 (O':V:O'')
clusters if move the two O\(^{\prime}\) interstitials to their nearest O\(^{\prime\prime}\) sites and form two V-O\(^{\prime\prime}\) pairs rather than the V-O\(^{\prime}\) ones. Figure 9 shows it might be local stable, in consistent with empirical calculations.\(^{42}\) The stabilization of O\(^{\prime\prime}\) by V-O\(^{\prime}\) pairs sited in the otherwise empty oxygen cages is unclear by figure \(\mathbf{8}\), but calculations show a V-2O\(^{\prime\prime}\) triple do stabilize O\(^{\prime}\) locally (O\(^{\prime}\)-V-2O\(^{\prime\prime}\)), as well as a V-2O\(^{\prime}\) can (O\(^{\prime\prime}\)-V-2O\(^{\prime}\)).

Thus we finally arrive at the conclusions that: (i) O\(^{\prime}\) or O\(^{\prime\prime}\) interstitials cannot exist by themselves; (ii) each O\(^{\prime}\) site must incorporate with two nearest oxygen vacancies, while O\(^{\prime\prime}\) can be stabilized by a V-2O\(^{\prime\prime}\) (O\(^{\prime}\)) triple. That means the possible clustering pattern for oxygen defects should only be: (a) V-3O\(^{\prime\prime}\) or V-4O\(^{\prime}\) isolated clusters, in the same manner of split-interstitial where several atoms sharing a single lattice site; (b) cluster chains of V-O\(^{\prime\prime}\)-V or V-2O\(^{\prime\prime}\)-V by sharing the vacancy sites. These chains should be closed to have all O\(^{\prime}\) interstitials locally stable whilst minimize the vacancy/interstitial ratio; (c) cluster of V-(2)O\(^{\prime\prime}\) chains terminated by two V-(2)O\(^{\prime}\) clusters at both of the extreme sides by sharing the vacancy sites. We call these small fractal clusters the Willis type cluster, including 1:2:2, 2:2:2, 4:3:2, 4:3:4 clusters and so on. However, their actual stability is still unknown which requires accurate knowledge about their formation free energies.

2. Phase diagram for clusters

In UO\(_{2+x}\), the positive formation energy of oxygen Frenkel pair and the small energy gain from interactions among interstitials (see figure 6) implies the only way to reduce the energy increment from creating vacancies is via vacancy-interstitial (V-I) interactions. Obviously the nearest V-I pairs contribute the most. Therefore the relative stability of clusters can be judged roughly by counting the number of nearest interstitials around each vacancy. For example in a 1:2:2 cluster, each vacancy has only two V-I pairs, while in 2:2:2 it has three and in 4:3:2 it is 3.3. That means 1:2:2 should be meta-stable, even though it can explain the concentrations measured by Willis in 1964.\(^{42}\) However, this data also can be explained by a larger cluster with 4 O\(^{\prime\prime}\) interstitials, namely, a 2:2:4 cluster where each vacancy has four V-I pairs. Willis type clusters are necessary in order to explain the large concentration of O\(^{\prime\prime}\) interstitials, which is impossible by cuboctahedral cluster only (belonging to pattern (b)). For example the data for crystal A done by Murray et al.\(^{45}\) obviously belongs to 2:2:2 clusters while crystal B should be a mixture of 4:3:2 and cuboctahedral clusters or a 6:4:2 cluster.

However, a big Willis type cluster is unfavorable since the disturbance to fluorite lattice is proportion to its size linearly. A similar situation holds for a loosely closed chain of the pattern (b). In this sense the most regular and close-packed defect cluster, the cuboctahedral cluster, takes the advantage of sharing the space with all vacancies and interstitials to minimize the damage to the matrix. Also, one fluorite cubic cell can accommodate one (or less) Willis type cluster or one cuboctahedral cluster. But the former provides only 2 excess anions while the latter provides 5. When composition \(x\) increased, cuboctahedral cluster has a big advantage over Willis type cluster, not to mention each of its vacancy has a number of V-I pairs greater than three. As for the clustering pattern (a), though there are 3 (V-3O\(^{\prime\prime}\)) or 4 (V-4O\(^{\prime}\)) V-I pairs for each vacancy, we can discard them at first since no experiments showed so high concentration for O\(^{\prime}\) interstitials.

It becomes evident when check the variation of O\(^{\prime}\)-O\(^{\prime\prime}\) ratio as \(x\) increased: around \(x = 0.11 \sim 0.13\), three different data sets were observed (0.08:0.16, 0.14:0.12, and 0.33:0.10), implying the occurrence of Willis type clusters. As \(x\) approaches to 0.25, however, this ratio increases drastically\(^{45,49}\) and shows the dominance of cuboctahedral clusters. Therefore, by taking the stability of point interstitial at low \(x\) into account, one concludes that there is a quasi-phase diagram for oxygen clusters in UO\(_{2+x}\), as shown in figure 10.\(^{50}\) To determine the exact geometry of ground clusters and their boundaries would be the center of future works in this field.

It is worthwhile to point out that such kind of defect clustering is not unique to uranium dioxide. According to the

\[
\begin{array}{|c|c|c|c|}
\hline
\text{point defect} & \text{Willis cluster} & \text{Willis cluster + cuboctahedral cluster} & \text{cuboctahedral cluster} \\
0.00 & 0.05 & 0.10 & 0.15 & 0.20 & 0.25 \\
\hline
\text{UO}_2 & \text{Composition (+x)} & \text{UO}_{0.9} \\
\hline
\end{array}
\]

FIG. 10: (Color online) A schematic phase diagram for oxygen defect clustering in UO\(_{2+x}\). The boundaries, however, are not clearly known.
formation energy of point defects, one can classify binary compounds into three classes: (A) all formation energies are positive, (B) only one of the formation energies is negative, and (C) both cation interstitial (vacancy) and anion vacancy (interstitial) have negative formation energies. There is no off-stoichiometry driven force in case (A), and disfavors extensive defect clustering. However the negative formation energies in the other two cases will drive the system to a non-stoichiometric composition where defect clustering becomes favorable. This is because the interaction among defects can lower the system energy greatly, and lead to a pure defect clustering (via a full vacancy-interstitial annihilation) or mixed defect clusters that contain both vacancy and interstitial. Also, the mixed cluster is possible only when the point defect with positive formation energy (vacancy or interstitial) has the function to stabilize the other defects in an energy favorable configuration (in a similar concept of the split-interstitial defect mechanism). Obviously UO$_2$ fulfills these conditions (see figure 2 and previous subsection) and belongs to case (B), where oxygen interstitial has a negative formation energy and clustering involves no uranium sites. On the other hand, case (C) contains clusters composed of both cation and anion defects, and might exhibit more complex behaviors.

G. Concentration of defects

1. Generalization of the PDM

The point defect model (PDM) was introduced by Matzkes$^{14}$ and Lidiard$^{15}$ to analyze the populations of defects in UO$_{2+x}$, where $x$ indicates the deviation from stoichiometry. This model is based on the hypothesis that the defects responsible for the deviation from stoichiometry in UO$_{2+x}$ are isolated point defects. However, it has been known for long that oxygen interstitials form clusters, and usually PDM performs poorly even at small $|x|^{12,13}$. Therefore it is worthwhile to generalize this model beyond the point approximation. Since traditionally defect concentrations are defined in a lattice model as the number of defects present divided by the number of available sites for the defect under consideration, the most general and elegant generalization of PDM would be cluster variation method (CVM)$^{24}$ which also bases on lattice gas model and computes cluster configurational entropy explicitly. The related effective cluster interactions can be determined by cluster expansion method (CEM)$^{52}$. For UO$_{2+x}$, at first sight it seems being a quaternary system ($V_O$, $V_U$, $I_O$, and $I_U$) and cannot be tackled by modern CVM and CEM techniques. But since defects on the uranium subsystem usually are isolated point defects that couple with oxygen subsystem via Schottky defects, in fact only oxygen defects need to be treated explicitly. However, in order to include O$^-$ and O" sites in the calculation, one has to use an extended lattice, which introduces another two difficulties.

The first one relates to the local stability of O$^-$ and O" sites, since these sites are not well defined and usually a full relaxation is required to get the optimized geometry. However, in most configurations they are not at the potential minimums and makes it impossible to include the relaxation effects in the ab initio CEM procedure. Fortunately, an algorithm proposed by Geng et al. can tackle this problem simply.$^{53}$ The second difficulty is that most configurations on the extended oxygen sublattice are unphysical, i.e., some distances among oxygen sites are too short to allowed. To exclude these unphysical configurations, one has to use loose clusters to expand the energy, which deteriorates the convergence of cluster expansion drastically.

If all non-negligible clusters are independent and uncorrelated, a simple approximation exists to calculate cluster populations. Two clusters are called independent if none of them is the other one’s sub-cluster (or loosely, cannot dissociate or combine into other clusters). This ensures all cluster concentrations are completely independent. Assume there are $M$ such kind of clusters under consideration, then the system free energy can be written as

$$F = \sum_{i=1}^{M} \rho_i (E_i + \kappa B T \ln \rho_i)$$

in the closed regime (in which the system cannot exchange atoms with the exterior). Here $E_i$ stands for the $i$-th cluster’s formation energy. Minimization this free energy with respect to each cluster density $\rho_i$ (under the condition that $x$ is fixed) gives

$$\rho_i = g_i \exp \left( \frac{-E_i}{\kappa B T} \right) ,$$

associated with the composition equation

$$x = f(\rho_1, \cdots, \rho_M).$$

In Eq. (6) the factor $g_i$ is introduced to account for the degeneracy if the cluster has internal freedom, while non-degenerated states can be treated as independent. This gives the internal entropy contributions and is the most significant difference between the independent clusters approximation (ICA) and PDM.
TABLE IV: Formation energies (eV) of point defects in UO$_2$: uranium and oxygen vacancies (U-Vac and O-Vac), uranium and oxygen interstitials (U-Int and O-Int), Frenkel pairs (O-FP and U-FP), and Schottky defect (S).

|       | U-Vac | O-Vac | U-Int | O-Int | O-FP | U-FP | S   |
|-------|-------|-------|-------|-------|------|------|-----|
| LSDA+U | 9.1   | 7.5   | 8.2   | −2.2  | 5.4  | 17.2 | 10.6|
| GGA+U  | 8.4   | 4.5   | 4.7   | −0.4  | 4.0  | 13.1 | 5.8 |
| GGA$^c$| 4.8   | 6.1   | 7.0   | −2.5  | 3.6  | 11.8 | 5.6 |
| GGA$^d$| 5.1   | 6.1   | 7.5   | −2.6  | 3.5  | 12.6 | 6.0 |
| LDA$^e$| 3.3   | 6.7   | 7.3   | −2.9  | 3.9  | 10.7 | 5.8 |
| LDA-LMTO$^{11}$| 19.1 | 10.0  | 11.5  | −3.3  | 6.7  | 30.6 | 17.1|
| Semi-empirical$^{14}$| 80.2 | 16.9  | −60.8 | −12.1 | 4.8  | 19.4 | 11.3|
| PDM estimates$^{14}$| −    | −     | −     | −     | −    | 3.0~5.8 | 9.5 | 6.0~7.0|

$^a$ this work, with 8 fluorite cubic cells
$^b$ with 8 fluorite cubic cells, Ref. 37
$^c$ with 2 fluorite cubic cells, Ref. 13
$^d$ with 1 fluorite cubic cell, Ref. 13
$^e$ with 2 fluorite cubic cells, Ref. 12

The PDM equations can be derived by considering only isolated point defect excitations (without internal structure): \( V_O, V_U, I_O \) and \( I_U \). In a closed system the particle numbers must be conserved, reduces the number of independent defect modes to three. On the other hand, the formation energy reference state for point oxygen and uranium defects usually are different, therefore one should instead use three independent combinations of these isolated defects to eliminate this ambiguity. The simplest candidates are oxygen and uranium Frenkel pairs and Schottky defect (or equivalently, anti-Schottky defect). Consequently, \( M = 3 \) and \( i = 1, \cdots, 3 \) corresponds to the isolated Frenkel pairs and Schottky defect, respectively. In this way Eq.(8) becomes

\[
\rho_{FP_O} = \exp\left(\frac{-E_{FP_O}}{\kappa_B T}\right) \equiv [V_O][I_O], \tag{8}
\]

\[
\rho_{FP_U} = \exp\left(\frac{-E_{FP_U}}{\kappa_B T}\right) \equiv [V_U][I_U], \tag{9}
\]

\[
\rho_S = \exp\left(\frac{-E_S}{\kappa_B T}\right) \equiv [V_O]^2[V_U], \tag{10}
\]

and the composition equation expressed in point defect populations

\[
x = 2([V_U] - [I_U]) + [I_O] - 2[V_O]. \tag{11}
\]

Eqs.(8-11) comprises the PDM equations exactly.

To include cluster effects, taking that in \( C_4 \) configuration as example, we need reinterpret the two interstitials as an isolated diagonal pair (\( dp \)). Assuming this interstitial pair is predominant over the point one, then Eq.(8) is replaced by

\[
\rho_{dp}[V_O]^2 = \exp\left(\frac{-E_{dp} - 2E_{V_O}}{\kappa_B T}\right), \tag{12}
\]

where two isolated oxygen vacancies have been introduced to eliminate the ambiguity in extrinsic defect formation energy. Also, the composition equation becomes

\[
x = 2([V_O] - [I_U]) + \rho_{dp} - 2[V_O]. \tag{13}
\]

with Eqs.(8) and (11) keep unchanged. This procedure can be extended to include other independent clusters easily.

2. Defect concentrations in PDM

In the point defect approximation, the formation energy of a Frenkel pair of the \( X \) species is given by

\[
E_{FP_X} = E_{V_X}^{N-1} + E_{I_X}^{N+1} - 2E^N \tag{14}
\]
FIG. 11: Analysis of the point defect model at a temperature of 1700 K. Variation of the concentrations of point defects with the deviation from stoichiometry $x$: hypostoichiometric regime (on the left) and hyperstoichiometric regime (on the right). Solid (respectively dotted and dashed) line indicate the concentration in oxygen interstitial (respectively oxygen vacancy and uranium vacancy). The concentration of uranium interstitial is negligible.

and for the Schottky defect (S) by

$$E_S = E_{V_U}^{N-1} + 2E_{V_O}^{N-1} - 3\frac{N-1}{N}E^N,$$

(15)

with $N$ the number of atoms and $E^N$ the total (or cohesive) energy in the defect-free supercell; $E_{V_X,I_X}^{N\pm1}$ the energy of the cell with the defect. Here we use $C8\pm1$ and $uC8\pm1$ to model the point defects, thus $N = 96$ and $E^N$ and $E_{V_X,I_X}^{N\pm1}$ can be obtained by timing 8 to the corresponding cohesive energies listed in table IV.

The formation energies of the defects obtained are listed in table IV. They are compared to the previous theoretical results \cite{11,12,13,37,54} and PDM estimates based on diffusion measurements \cite{14} Note that the GGA+U employed the same $U$ parameter as in this work. A detailed comparison of its results with LSDA+U can be found in Ref. [2]. Despite it produced a similar band gap and local magnetic moment as LSDA+U, it predicted a big lattice constant $\sim 5.55 \AA$. By figure 7 we know this would lead to an underestimation of the oxygen interaction with the matrix. Table IV proves this by showing a smaller absolute value of the oxygen interstitial and vacancy formation energies than any other calculations. However, this failure is not from GGA but the parameter of $U$.\cite{55} Besides, this $U$ also underestimates the formation energy of uranium interstitial greatly, implying one needs to fitting an own $U$ value for GGA functional separately.

The improvement of LSDA+U over the pure GGA or LDA results is significant. Both the latter underestimate the formation energy of uranium vacancy by about 2 times, and 10% $\sim$ 20% for oxygen vacancy. By the lump, LSDA+U corrects the energy for O-FP by a 50% and 38%, a 46% and 61% for U-FP, an 89% and 83% for Schottky defect over GGA and LDA, respectively. This correctness makes our LSDA+U results the first ab initio defect formation energies that predict the predominance of oxygen defects within a broad enough stoichiometric range over uranium ones (For the performances of LDA or GGA formation energies and the PDM anticipation, please see Refs. [12,13]).

The defect concentrations, or equivalently populations, calculated with PDM equations are shown in figure 11. An arbitrary temperature of 1700 K is chosen. We see oxygen interstitial dominates when $x > 0$ while it is oxygen vacancy when $x < 0$. At $x \sim 0$, O-FP overwhelms. This picture is in a good agreement with diffusion measurements interpreted by PDM,\cite{14} but different from neutron diffraction data where non-negligible oxygen vacancies were observed when $x > 0$.\cite{4,5,6,7,8,48} The population of oxygen vacancy predicted by PDM is too low to be true. To increase this population in the regime $x > 0$, one needs to take clustering effect into account.
3. Defect concentrations with independent clusters approximation

Assume the oxygen diagonal pair in $C_4$ is dominant over the single interstitial, one can calculate the clustering effect formally. It is not a promising assumption due to the small energy difference between them. While it can be used to analyze the influence of pure interstitial clusters that occupied only the octahedral sites on the vacancy populations (they should have similar effects). Also it serves to show how the independent clusters approximation works out.

Using the defect formation energy of $C_4$ and Eqs. (9, 10, 12 and 13), we calculated the defect populations following the same manner as PDM, the result is presented in figure 12. Note here that $\rho_{pd}$ turns out to have the same numeric value as $[I_O]$. We see that this pure clustering mechanism do decrease the oxygen interstitial population, but that of oxygen vacancy in the $x > 0$ regime is still too low. Another problem raised here is the population of uranium vacancy is closely pinned on that of the oxygen interstitial. It is not what we wanted. Roughly, figure 12 suggests clusters associated with oxygen vacancies is necessary in order to enhance the latter’s concentration greatly in $x > 0$ regime and to pin on that of oxygen interstitial, as implied by the neutron diffraction measurements.

IV. CONCLUSION

In summary, we performed a comprehensive calculation on defect properties in UO$_{2\pm x}$ with LSDA+U method. The volume changes induced by defects and their formation energies were computed accurately. Analysis of these energies for a series configurations concluded that defect clustering is unavoidable when $x \geq 0.03$, compatible with experimental fact. Atomic charge calculations in Bader’s definition, however, showed the difficulty to oxidize uranium to U$^{6+}$ and the charged oxygen apt to losing its electrons, against common expectation. As the simplest interstitial cluster, oxygen dimer behaviors in a manner similar to a normal oxygen in energetics and charge state. It was identified as ionic dioxygen molecule with two excess electrons. Static and vibrational free energy calculations, however, showed it quite unstable and might only be a transient state during oxidation process.

Oxygen dimer is the extreme case for interstitialcy diffusion of oxygen, which may induce a charge fluctuation with a magnitude less than 0.2 $e$. It also presents as a special case for Willis O’ site occupancy under stretch. The stabilization mechanism for this site under ambient conditions, however, is attributed to a V-2O’ (O’) triple by the local stability analysis. Also, O’ site is stabilized only by the nearest oxygen vacancy pair. This comprises the basic clustering pattern for defects in UO$_{2\pm x}$: play with the four building blocks (V-(2)O’ and V-(2)O’-V) by sharing the vacancy sites. The actual stability of clusters should be judged by the formation energies, which beyond the scope of this paper and we prefer to future work. A quasi phase diagram for defect clusters vs composition was also proposed to explain the observed population ratios of O’ and O” sites, which of course requires further refinement step by step when more calculations and experimental data are available.
The formation energy of Frenkel pairs and Schottky defect calculated with LSDA+U have been improved more than 50% over the GGA and LDA results. With these energies and the point defect model, we first time showed the predominance of oxygen defects by first principles. Finally we generalized the PDM to independent clusters approximation that allows us to compute the population of clusters, and revealed the necessity to move on to Willis type clusters.

Acknowledgments

This study was financially supported by the Budget for Nuclear Research of the Ministry of Education, Culture, Sports, Science and Technology of Japan, based on the screening and counseling by the Atomic Energy Commission.

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There may have other complex mechanisms for oxygen adsorption and surface reconstruction that might modify the potential surface and then the numerical values considerably, but this picture still holds for deep-layers in a qualitative sense. This argument is also supported by Ferguson and McConnell’s report of about $-230 \text{kJ mol}^{-1}$ ($\sim -2.38 \text{eV}$) heat is released out in the chemisorption of molecular oxygen onto the surface of UO$_2$ during the initial stages of the reaction, as quoted in Ref.[38], being comparable to the energy that would be released if decompose an oxygen dimer in UO$_2$ matrix.

There no temperature influence is considered. A more realistic description should include this effect since usually temperature will alter cluster populations greatly.

Similar phenomenon also happened in cerium oxides, where the GGA+U fails to reproduce the experimental structure properties and vacancy formation energy very well within a wide range of $U$, indicating there might have some slight incompatibility between DFT+U and GGA formalism [see D. Andersson, S. I. Simak, B. Johansson, I. A. Abrikosov, and N. V. Skorodumova, Phys. Rev. B 75, 035109 (2007).]