Interplay of defect cluster and the stability of xenon in uranium dioxide by density functional calculations

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Abstract

Self-defect clusters in bulk matrix might affect the thermodynamic behavior of fission gases in nuclear fuel such as uranium dioxide. With first-principles LSDA+\textit{U} calculations and taking xenon as a prototype, we find that the influence of oxygen defect clusters on the thermodynamics of gas atoms is prominent, which increases the solution energy of xenon by a magnitude of 0.5 eV, about 43\% of the energy difference between the two lowest lying states at 700 K. Calculation also reveals a thermodynamic competition between the uranium vacancy and tri-vacancy sites to incorporate xenon in hyper-stoichiometric regime at high temperatures. The results show that in hypo-stoichiometric regime neutral tri-vacancy sites are the most favored position for diluted xenon gas, whereas in hyper-stoichiometric condition they prefer to uranium vacancies even after taking oxygen self-defect clusters into account at low temperatures, which not only confirms previous studies but also extends the conclusion to more realistic fuel operating conditions. The observation that gas atoms are ionized to a charge state of \textit{Xe}^{+} when at a uranium vacancy site due to strong Madelung potential implies that one can control temperature to tune the preferred site of gas atoms and then the bubble growth rate. A solution to the notorious meta-stable states difficulty that frequently encountered in DFT+\textit{U} applications, namely, the quasi-annealing procedure, is also discussed.

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I. INTRODUCTION

The thermodynamics of fission products in uranium dioxide has been a focus of considerable experimental and theoretical attentions in nuclear industry. Xenon as the most important fission gas is one of them. Concern has been particularly centered on xenon’s role in fuel swelling—that could increase the pressure on the cladding of the fuel rod under irradiation and lead to rupture. A similar risk also exists for the container of nuclear waste in storage conditions. This has accordingly led to a desire to obtain a greater understanding of the basic processes governing the migration and trapping of xenon within the fuels. 1–5

Previous theoretical studies on xenon behavior employed interatomic potentials such as shell model. 1–3 This method provided qualitative understanding of gas properties. However, since shell model has severe transferability difficulty, 6 the reliability of its results requires further verification by other methods. Application of quantum mechanics to this problem was available only recently and focused mainly on single gas atoms that occupying point vacancies and Schottky sites. 7–12 In uranium dioxide, however, oxygen defect clusters dominate and the interplay of them and fission gases might be the key to correctly understand the subtle material behavior. For example, in hyper-stoichiometric regime of UO$_{2+x}$ where $x > 0$, oxygen self-defect cluster—the cub-octahedron (COT) cluster dominates when temperature is relatively low. 13–17 There is a big cavity at the center of COT, which can either be empty (denoted as COT-v), or be filled by additional oxygen and forms COT-o cluster, or be filled by xenon atom and becomes COT-xe. Furthermore, existence of COT-v and COT-o clusters changes the concentrations of all other defect traps that the gas atoms can incorporate with. Such kind of direct and indirect effects of oxygen clusters have not yet been investigated. Big cavity also can be found at uranium vacancy or tri-vacancy (tri-V, a kind of bound Schottky). We will show that xenon atoms are prone to occupying these traps and become xenon-trap aggregates. This incorporation behavior not only reduces elastic strains that imposed on the bulk matrix but also changes the development of intra-granular bubbles, and thus is possible to alleviate the fuel swelling that suffered from fission gases.

Energetics of xenon in defective UO$_2$ was modeled in a $2 \times 2 \times 2$ supercell consisting of eight fluorite cubic unit cells. Periodic boundary conditions and the density functional theory in local spin density approximation with Hubbard correction to the on-site coulombic repulsion of the localized uranium 5$f$ orbitals (LSDA+ $U$) were employed to com-
ute the total energy. All structures were fully relaxed until residual forces less than 0.01 eV/Å. Details of the computational setup and the validation of the method are referred to Refs. [17,21,22]. Particularly the LSDA+U approach has been applied to perfect and self-defective UO$_2$ successfully, and yielded results in good agreement with experiments. Oxygen defect clustering and the relevant thermodynamics have also been well described by this method.

In next section we will discuss a solution to the notorious meta-stable states problem that frequently encountered in DFT+U applications. This approach was developed in our previous calculations. Though it lacks a rigorous theoretical basis and cannot guarantee that the true ground state can always be achieved, we found that it is effective to reduce the frequency of encountering high-lying meta-stable states and thus improves the reliability of the computational results. In Sec. III and IV a systematic analysis of the electronic structure and energetics of xenon atoms that incorporating in nuclear fuels will be given, as well as the influence of oxygen defect clustering on the incorporation energies, the solution energies and the relevant thermodynamics of xenon gas. In section V a comparison with other theoretical results will be discussed, followed by a summary.

II. QUASI-ANNEALING PROCEDURE

A. Theoretical argument

DFT+U formalism improves the performance of density functional theory on strongly correlated electronic system by including a Hubbard correction to the on-site coulombic repulsion in a semi-empirical manner. The cost is, however, introduced a lot of local minima on the energy surface that obstructing energy minimization process, and making electronic optimization algorithms get stuck in meta-stable states. Monitoring the occupation matrices (MOM) of the localized $f$ orbitals can solve this problem partially by varying their initial values to search for the lowest state. But this option is not generally available in most DFT packages. Also the approach is a try and error method, which cannot ensure that the global minimum has already been obtained before all possible occupation matrices have been tried. Another concern about MOM is the computational cost. If spin degree is not considered, there are $C_7^n$ different ways of filling $n$ electrons in seven $f$ levels diagonally. The
FIG. 1: Schematic illustration of the electronic optimization process in quasi-annealing procedure, where fluctuations of potential surface (here from the solid to the dashed, and then back to the original solid contours) due to ionic drifts drag the minimizing path from 1, 2, 3, 4, 5 to 1, 2, 3, 3', 4', 5, thus circumvents possible meta-stable states on the original route.

number of different nondiagonal occupation matrices is much larger, but we can reduce it to several times of the number of the diagonal case by assuming that all other occupations are insignificant. Thus for each atom there are $mC^m_n$ different ways to fill the $f$ levels, with $m$ less than ten. It is also the total number of the runs that are required for each calculation if the simulation cell contains only one symmetry inequivalent atom. Unfortunately the symmetry of defective system is usually low, and has several non-equivalent atoms (say, $k$) with localized $f$ electrons. In such a case a total number of $(mC^m_n)^k$ runs are necessary for each calculation. For UO$_2$, $n$ equals 2 and $m$ can take 3, thus gives about 60 different occupation matrices for each uranium. If point defects are concerned, there are at least two non-equivalent uranium atoms, and the number of the total runs would increase to 3600. For defect clusters, $k$ should be greater than 3 and it requires millions of runs for each calculation to get the final result. This is a huge burden even for modern supercomputers.

In a classical system, the meta-stable states difficulty can be tackled satisfactorily with annealing procedure. Namely, to remove the thermal kinetic energy of a system gradually and slowly so that all low-lying states have been visited before picking out the ground solution. Similar concept can be applied to electronic system. The basic idea is to shake or heat the electronic system with a spurious energy noise to help it overcome the energy barriers. We call this method the quasi-annealing (QA) procedure.

The theoretical basis is that the electronic energy is a functional of the electron density
\( n(r) \), which is in turn a unique functional of the external potential \( v(r) \). One can then convey the spurious noise from the ionic subsystem to the electronic subsystem via \( v(r) \). It amounts to \( \int \Delta v(r)n(r)dr \), where \( \Delta v(r) \) is the fluctuation of the external potential. By switching off this spurious energy gradually, one can extract the ground state in a similar way as its classical counterpart. Alternatively, we can understand the mechanism of removal of the meta-stable states in QA procedure by tracking the electronic minimization process: the potential fluctuations alter the minimization path iteratively, thus being capable of avoiding any possible meta-stable states that lying on its route, as illustrated in figure 1.

In practice, one might exploit the residual energy of the minimization process. The energy uncertainty \( \delta E \) due to non-convergence of the self-consistency field (SCF) gives a quasi-random fluctuation in ionic forces, which in turn leads to a gaussian distribution of the ions with respect to their physical positions. The potential fluctuation \( \Delta v \) arising from this ionic drift eventually heats the electronic system up. Generation of \( \Delta v \) from the forces can be done with standard structure optimization algorithms. That is, one iteratively relaxes the ionic structure with an electronic state having a SCF tolerance of \( \delta E \). In this realization, the only one parameter—the residual energy in SCF—controls the spurious noise in the electronic system. Its value should be large enough at the beginning so that the electronic system can travel freely in the phase space. By decreasing \( \delta E \) gradually, one converges the electronic system down to the ground state.

The merits of QA are not just that it can be used to tackle the meta-stable states. By coupling with ionic relaxation, one can optimize the electronic and ionic states simultaneously. It reduces the total computational cost dramatically when structure optimization is also required, especially when DFT+\( U \) formalism is employed where the SCF convergence is very slow. To avoid ions drifting too far away from the target configuration, one needs to restore the structure after some ionic steps. Usually allowing cell volume and shape to vary improves the performance, because it not only extends the searching space, but also shakes the system globally and breaks the symmetry imposed by the Bravais lattice, which is one of the main reasons that lead to high-lying meta-stable states in strongly correlated system.\(^{24,25}\)
FIG. 2: (Color online) Main meta-stable states in PuO$_2$ and the performance of quasi-annealing procedure, which predicted the lowest total energy.

B. Validation

The QA procedure is summed up as follows, where in each step the computation restarts from the wave-function that was generated in its previous step.$^{28}$

1. Switch off symmetry, set appropriate values for SCF tolerance $\delta E$ and ionic relaxation step size $\delta r$.

2. Employ standard ionic optimization algorithms to evolve the structure.

3. Reduce $\delta E$ and $\delta r$ slightly, restore the structure, goto step 2 and repeat the procedure until $\delta E$ reaches the target precision.

4. Conduct a standard SCF iteration.

5. Slightly distort the structure, goto step 2 and repeat the whole process until no lower state can be found.

At first we discuss the performance of QA in a perfect fluorite cubic cell of PuO$_2$ (with 12 atoms) that ordering in 1k antiferromagnetic configuration with GGA+$U$ method. The PAW pseudo-potentials and PBE exchange-correlation functional were used. The Hubbard parameters were 4.0 eV for $U$ and 0.7 eV for $J$. A cutoff of 400 eV was adopted for the kinetic energy of the plane wave basis, and 63 irreducible $k$-points were used to sample the Brillouin zone. The lattice parameter was fixed at 5.45 Å. It should be pointed out that
this setup was only for PuO$_2$. All the following defects calculations were conducted with LSDA+$U$ method as detailed in Sec.I. Here we chose PuO$_2$ because this system has very stable meta-stable states. For example if the cubic symmetry ($O_h$) is imposed onto the system, one always obtains a meta-stable state having a total energy of $-125.282$ eV, no matter what the initial condition of the calculation is. This is different from UO$_2$ where the symmetry-induced meta-stable state can be removed easily. In PuO$_2$, however, one has to switch off the symmetry in order to get rid of this state. As shown in figure 2, switching off the symmetry lowered the energy by $1.69$ eV. But this is far from being the ground solution. Adiabatically switching on the Hubbard on-site interactions, namely, increasing the $U$ and $J$ parameters from zero slowly, further reduced the total energy about $0.16$ eV. The QA procedure, in contrast, predicted a much lower energy. A total number of six independent QA runs were performed. The results were similar and the standard deviation $\sigma$ (scattering of the data) was $0.006$ eV. On the other hand, direct SCF calculations have a standard deviation of two orders larger than QA. This suggests that the electronic system has gotten rid of high-lying states and converged closely to the ground solution in QA. The best result we ever had is $-127.684$ eV.

It is helpful to compare QA results directly with MOM. We thus performed a GGA+$U$ calculation on perfect UO$_2$ with the same setup as in Ref.[27]. The only difference is that we used a $500$ eV cut-off energy for the plane-wave basis set and a $5 \times 5 \times 5$ $k$-point mesh instead of the $600$ eV cut-off and the $6 \times 6 \times 6$ $k$-point mesh that were used in that work. This difference should have little influence on the final result since the total energy has already been converged well with this setting of parameters. After a fully relaxation of the ionic structure, QA gave a total energy of $-117.095$ eV, lower than MOM’s $-116.505$ eV for fluorite structure and $-116.712$ eV for Jahn-Teller distorted geometry (see table V in Ref.[27]). We cannot state that QA outperforms MOM, but it is obvious that an incomplete implementation of MOM as done in Ref.[27] does not necessarily lead to a ground state solution.

Figure 3 demonstrates the improvement of QA procedure against direct SCF calculations for a set of defects in UO$_2$, including point oxygen interstitial, oxygen vacancy, uranium vacancy, split quad-interstitial, xenon atom that incorporated in a tri-vacancy site, and COT-o cluster. We found that direct SCF calculations always stopped at high energy states, with an energy distance about $0.3$ eV to the QA results, regardless of the defect
FIG. 3: Total energy difference between direct SCF and QA calculations of some type of defects in UO$_2$, where the QA results are at the zero level. All direct SCF calculations were performed using the fully relaxed structures.

It is worthwhile to point out that these direct SCF calculations were performed on structures that already optimized by QA procedure, and the cubic symmetry of the lattice had been switched off. One interesting example is about the stability of oxygen defect clusters. Andersson et al. did LSDA+$U$ calculations on the stability of defect clusters in UO$_2$ without QA treatment. The results were controversial: they predicted that the split quad-interstitial ($\text{V-3O}^{\prime\prime} \text{O}^{\prime\prime}$)$_2$ had an energy lower than COT-o cluster. Here we denote the split quad-interstitial by the symbol ($\text{V-3O}^{\prime\prime} \text{O}^{\prime\prime}$)$_2$ because it is actually a linear combination of two basic clusters—$\text{V-3O}^{\prime\prime}$, an oxygen vacancy surrounded by three Willis O$^{\prime\prime}$ interstitials. A careful re-computation of the energetics of these two clusters with QA procedure, however, gave a different picture. We found that Andersson et al.’s energy of ($\text{V-3O}^{\prime\prime} \text{O}^{\prime\prime}$)$_2$ was almost the same as QA. But their value of COT-o was much higher than that of QA (in terms of formation energy with respect to the same reference state, $-10.38 \text{ eV}$ vs. $-12.41 \text{ eV}$). A direct SCF run with QA-optimized structure led to a meta-stable state with an energy of 0.16 eV higher than that of QA, and was much lower than Andersson et al.’s original result. A re-check calculation using the same setup as theirs also failed to reproduce their results. According to the variational principle of energy, we guess that their calculation of COT-o cluster might have stopped at a meta-stable state. Unfortunately we cannot identify it without reproducing their electronic state successfully.
Now we have two approaches that can tackle meta-stable states, i.e., MOM and QA. In the case of perfect UO$_2$, though primary MOM calculations did not predict a lower state than QA, it does not mean QA truly achieved the ground state. We know that annealing procedure does not perform well when there are a lot of local minima that have the same amplitude and the same width. Thus it cannot state that the meta-stable states problem has been solved satisfactorily by QA. However, QA is effective to remove high-lying meta-stable states and to bring the system down to one of the low-lying states that have small amplitude. From the experience of MOM$^{25,26}$ we estimate the absolute error in QA might be less than 0.1 eV. The relative energy difference between systems would be much better and at an order of $2\sigma$ due to error cancelation. In practice, QA is an effective method to reduce data scattering and to improve the reliability of the calculated energetics.

In brief, when the system is small and the computer resource is enough so that allowing to repeat the calculation many times, MOM is a good choice. With this method one can get explicit information of how the meta-stable states distribute. On the other hand, QA optimizes ionic and electronic degrees simultaneously. Thus if atomic structure optimization is desired, QA would outperform MOM, especially for large systems. All of the following calculations have been treated by QA procedure to improve the reliability of the results.

**III. FORMATION ENERGY AND INCORPORATION ENERGY**

The formation energy of a defect $D$ that has $n$ excess oxygen atoms is defined as

$$E_f^D = E_{D}^{coh} - E_{per}^{coh} - \frac{n}{2} E_{O_2},$$

and for a defect with $m$ excess uranums is

$$E_f^D = E_{D}^{coh} - E_{per}^{coh} - mE_{\alpha U}.$$  \hspace{1cm} (2)

Here the cohesive energy $E_{D}^{coh}$ of a defective structure is calculated from its total energy by subtracting the isolated spin-polarized atomic contributions, and $E_{per}^{coh}$ is the cohesive energy of the corresponding structure without defect; $E_{O_2}$ is the binding energy of a neutral dioxygen molecule; and $E_{\alpha U}$ is the cohesive energy per atom in the metallic $\alpha$-U phase.$^{21}$

For tri-vacancy that keeps the UO$_2$ composition unchanged, the formation energy is given by

$$E_f^{tri} = E_{tri}^{coh} - \frac{N - 1}{N} E_{per}^{coh},$$

\hspace{1cm} (3)
TABLE I: LSDA+ $U$ results for structural and energetic properties of defects in uranium dioxide: defect traps [the tri-vacancy (tri-V), the octahedral interstitial site (Int.), the uranium site (U), and the oxygen site (O)] and xenon-trap aggregates [COT-xe—xenon in COT cluster, Xe(X)—Xe in trap X], respectively. $\Delta V$ is the defect induced volume change that averaged to per fluorite cubic cell (over eight cells totally). $E^f$ is the formation energy, $E^i$ is the incorporation energy, and $q$ is the Bader effective charge of xenon. The data of three oxygen self-defects are also included for reference, see Ref.[17] for details.

|                | COT-xe | Xe(Int.) | Xe(U) | Xe(O) | Xe(tri-V) | tri-V | COT-v | COT-o | O$_i$ (Int.) |
|----------------|--------|----------|-------|-------|-----------|-------|-------|-------|-------------|
| $\Delta V$(Å$^3$) | 0.79   | 3.74     | 0.97  | 3.99  | 1.40      | 0.54  | -0.14 | -1.61 | -0.29       |
| $E^f$(eV)       | -4.08  | 9.75     | 12.92 | 15.06 | 5.17      | 4.99  | -7.18 | -12.41| -2.17       |
| $E^i$(eV)       | 3.10   | 9.75     | 3.87  | 7.53  | 0.18      |       |       |       |             |
| $q(|e|)$        | 0.20   | 0.26     | 0.96  | 0.14  | 0.09      |       |       |       |             |

where $N$ is the total number of UO$_2$ formula that contained in the perfect cell. The incorporation energy of xenon is defined by

$$E^i = E^{\text{total}}_{Xe(X)} - E^{\text{total}}_X - E_{Xe},$$

(4)

where $E^{\text{total}}_{Xe(X)}$ is the total energy of a cell in which the xenon atom is at the trap site $X$, $E^{\text{total}}_X$ is the total energy of the same cell containing only the trap $X$, and $E_{Xe}$ is the total energy of an isolated xenon atom. If taking xenon-trap aggregate as a single defect complex, one can define its formation energy similar to Eq.(1) or (2) except that here $E_{Xe}$ also should be deducted. Numerically it is equal to the sum of the trap formation energy and the incorporation energy of xenon at that trap.

The calculated results of structure and energetics of various trap sites and xenon-trap aggregates in UO$_2$ are listed in table I. The tri-vacancy (tri-V) is a kind of bound Schottky defect that has the same geometry as shown in figure 3(e) of Ref.[1], i.e., a pair of oxygen vacancies that binding with one of its nearest uranium vacancies. It is believed that this geometry has the lowest energy. Defects V-4O$''$, V-3O$''$ and (V-3O$''$)$_2$ are not included here. The trap in these clusters is too small to accommodate xenon atoms: introducing one xenon atom completely destroys the trap geometry and the aggregate becomes unstable. In addition, previous investigations showed that these defects have insignificant concentration...
The energetic information in table I is interpreted as for isolated defects. This is appropriate for point defects since the simulation cell is large enough for them. But for extensive clusters such as COT, the cell is not large enough and the interactions with their images that arising from the periodic boundary conditions might be remarkable, with dipole-dipole interactions as the leading contribution. Therefore the obtained energy is more close to the value of an ordered configuration of the clusters at the corresponding concentration. Using this energy to describe diluted clusters is theoretically questionable. But the quality will become better and better as the concentration gets increasing. Fortunately, COT clusters only appear in the hyper-stoichiometric regime and have high enough concentrations, which implies that the size-effects of COT clusters might have little impact on our discussion here.

COT-xe has the lowest formation energy (as defined above) in all of the defects considered here, followed by Xe(tri-V), Xe(Int.), Xe(U), and Xe(O). The high formation energy of Xe(U) is due to the contribution of the uranium vacancy trap, whereas the low value of COT-xe is because of the excess oxygens, with each one contributing about $-2 \text{ eV}$. Thus it is helpful to divide the xenon-trap aggregate formation energy into two parts: the trap formation energy and the energy that is required to incorporate xenon atom into the pre-existing trap. The latter is called incorporation energy and is also listed in table I. We see that the most easy trap for xenon to incorporate with is tri-vacancy, followed by COT cluster and uranium vacancy.

It is understandable that rare gases such as xenon and krypton need a big space for them to be accommodated in the fuel matrix, and gas-fuel incorporation is usually accompanied with drastic swelling of the latter, especially when the gas atoms occupy mainly the octahedral sites [Xe(Int.)] or oxygen vacancies [Xe(O)]. But if most of the gas atoms go into pre-existing traps that have comparable size, for example uranium vacancies, tri-vacancies or COT clusters, the resulting fuel deformation will be much small, as can be perceived from the $\Delta V$ row of table I. This primary analysis indicates that xenon prefers to COT clusters or uranium vacancies instead of octahedral sites or oxygen vacancies. From table I we can see that the incorporation energy is as high as 9.75 eV (7.53 eV) when xenon is at an octahedral site (oxygen vacancy), and decreases to 3.1 eV when goes into COT cluster. This suggests that there is a deep local minimum on the energy surface at COT center, which will drive xenon atoms from octahedral sites and oxygen vacancies into COT clusters. Similar
FIG. 4: (Color online) Formation energy of various defect arrangements in UO$_2$: (A) a system with one xenon atom and four excess oxygens, and (B) with one more excess oxygen.

Conclusion holds for tri-vacancy and uranium vacancy.

Figure 4 illustrates in details how this takes place in UO$_2$, where the energy variation for different combinations of xenon atom and excess oxygens is given. For clarity we assumed here that point xenon occupies an octahedral site. The discussion is similar if it is at an oxygen vacancy. Point oxygen interstitials are also assumed occupying octahedral sites. In figure 4(B) the competition between COT-v and COT-o clusters is demonstrated. The energy cost is about 1.5 eV to bring four point oxygen interstitials together to form a COT-v cluster. The energy gain is 6.5 eV when the xenon atom goes into COT-v center from an octahedral site. Most of this part of energy gain is from the elastic contribution. Similarly, swapping the central oxygen of COT-o with a xenon atom reduces the total energy by 3.5 eV. The preference of xenon to COT trap is thus evident in both cases. It is easy to understand this by size effects: the atomic size of xenon is larger than the octahedral site, thus a drastic lattice distortion occurs when xenon atom occupying an octahedral site. But it is not when xenon is in COT clusters. Therefore as long as there are COT-o or COT-v clusters, xenon atoms will combine with them instead of occupying octahedral sites or oxygen vacancies.

Note that there are two kinds of incorporation process for COT-xe: (a) a direct combination of a xenon atom and a pre-existing COT-v cluster; (b) swap a xenon atom with the central oxygen of a COT-o cluster. In the first case the total xenon-trap aggregate formation energy is $-4.08$ eV, with a xenon incorporation energy of $3.10$ eV, and a trap formation
FIG. 5: (Color online) Density of states of O $2p$ (black) and U $5f$ (blue) orbitals that projected onto the defect atoms in COT-o (upper panel), COT-v (middle panel), and COT-xe (lower panel), respectively. Contribution from the central atom (oxygen in COT-o and xenon in COT-xe) is marked by red lines. The dotted vertical line indicates the Fermi level.

energy (COT-v) of $-7.18\,\text{eV}$, as listed in table II. In the latter case, however, the total formation energy is $-6.25\,\text{eV}$ (with $-2.17\,\text{eV}$ contributed by the point oxygen interstitial), with the xenon incorporation energy of $6.16\,\text{eV}$, and the trap formation energy (COT-o) of $-12.41\,\text{eV}$. Therefore in the case (a) the incorporation is easy but the available number of COT-v trap is rare, whereas in the case (b) the situation is just opposite.

To understand this kind of incorporation behavior, the mechanism of the energy variation from COT-o to COT-v is the key. Figure 5 shows the electronic density of state (DOS) of oxygen $2p$ and uranium $5f$ orbitals that projected onto the cuboctahedron atoms of COT-o, COT-v and COT-xe, respectively. The red lines indicate the contribution from the oxygen or xenon atom that occupies the cluster center, and the dotted vertical line indicates the Fermi level. There are three significant features: (1) the distribution profile of the O $2p$ DOS within the main valence band, (2) the localized U $5f$ states just below the Fermi level, and (3) the interplay of the localized xenon state and the valence band.

In COT-o, the central oxygen not only hybridizes itself with U $5f$ states directly, but also enhances the overlapping of the main O $2p$ and U $5f$ orbitals near the upper band edge. As a result, the localized U $5f$ states just below the Fermi level are absorbed into the valence band. This makes COT-o stable in energetics. In contrast, in COT-v and COT-xe, the hybridization with localized U $5f$ states is insufficient. Though a weak anti-bond is
formed by partial overlapping, a highly localized state still presents near the Fermi level. This feature and the fact that O 2p DOS distributes more on the upper part in the main valence band reveal the electronic origination of the energy increase from COT-o to COT-v. Different from oxygen whose effect is at the upper band edge, xenon in COT-xe affects mainly the lower edge of the valence band. As shown in the lower panel of figure, xenon interacts with itinerant O 2p and U 5f orbitals weakly, splitting the main valence band into a minor localized bonding state and a major anti-bonding band that is dispersive. The latter is then pushed to higher energy and is the main contribution to the energy difference between COT-xe and COT-v. Since this band shift keeps most features of the valence band unchanged, xenon effects on energetics is thus mainly mechanical.

Table I also lists the Bader effective charge of xenon in various traps at the last row. We see that except tri-vacancy in which xenon is charge neutral, all other traps have a tendency to ionize xenon atom. Usually the degree of this ionization is small when the gas atom is in COT cluster, oxygen vacancy, or octahedral site. This is because of the relatively electron-rich environment of these traps. But in the case of Xe(U), one electron has been completely peeled off due to the strong Madelung potential of the periodic lattice at the uranium vacancy sites. It is a competition process between the electron affinity of the trap and the ionization energy of the gas atom. Thus the ionization does not lead to a large energy increase. The observed ionization of Xe to Xe+ confirms Grimes et al.’s prediction with shell model. This charge transfer has important implication on gas bubble growth rate. It is believed that gas bubble grows by accumulation of point xenon impurities via diffusion. Positively charged gas atoms expel each other strongly due to the electrostatic interactions. Thus they cannot approach together. This means that inert gas bubble cannot initiate from uranium vacancies. In agreement with shell model results, we found that fission gas bubbles can only start from neutral tri-vacancy sites. As will be discussed below, this property makes temperature and the chemical composition being effective parameters to tune the growth rate of bubbles.

IV. SOLUTION ENERGY AT FINITE TEMPERATURES

With only the information of formation energy and incorporation energy that discussed in the previous section, it is difficult to evaluate what kind of trap the gas atoms prefer to
FIG. 6: Solution energy of xenon at various traps in UO$_2$ at 1500 Kelvin

at finite temperatures. For example COT-xe has the lowest trap formation energy—which suggests a high concentration of the trap—but the incorporation energy is high. Thus it is not necessarily the favored one, because the preferred site should be a combination result of the available number of the trap sites and the degree of incorporation difficulty. We knew from previous investigations on oxygen clustering behavior in UO$_2$ that in hypo-stoichiometric regime (UO$_{2-x}$) oxygen vacancy is the major defect, and in UO$_{2+x}$ there is a transition from point oxygen interstitials to COT-o clusters with an increase of the composition. That is, oxygen vacancy and COT-o are the most available traps in UO$_2$. On the other hand, the concentrations of COT-v, uranium vacancy and tri-vacancy are one order smaller, but they have lower incorporation energies. Therefore a delicate analysis is required in order to get the final answer.

Theoretically, the probability for a gas atom to be trapped in a specific site is proportional to the product of the trap concentration $\rho_t$ and the probability to incorporate the gas atom into one of these traps. In this way one can define the solution energy as

$$E^s = -\kappa_B T \ln \rho_t + E^i,$$

(5)

which gives the probability of trapping one gas atom to a specific trap by $\exp(-E^s/\kappa_B T)$. Here $\kappa_B$ is the Boltzmann constant and $T$ is the temperature. The first term in Eq. (5) gives the effective formation free energy of the trap and the second term is the incorporation energy. With independent cluster approximation, one can evaluate the trap concentration as a function of temperature and chemical composition in the closed regime. This approximation holds valid as long as there has no explicit overlapping or strong interactions.
among traps. Note that the temperature effect considered here is only the statistical effect on trap concentrations. Contribution from lattice vibrations on defect formation energy can be included straightforwardly, but here we did not take this into account because we focus mainly on the fundamental incorporation behavior of single gas atoms.

Calculated solution energies of xenon at various trap sites at 1500 K are shown in figure 6. For tri-vacancy and octahedral interstitial sites, the solution energies are independent of composition since creation of these traps does not change the stoichiometry. The stoichiometric effects on oxygen vacancy and uranium vacancy are opposite. There is a step-like jump near the stoichiometry. Far away from that composition, the variation of solution energy flats out. In hypo-stoichiometric regime, tri-vacancy has the lowest solution energy. All other traps have a solution energy at least 3 eV higher, and the physical picture is clear and trivial. In the other side of the stoichiometry, however, thermodynamic competition becomes important. The solution energy of xenon at tri-vacancy sites is 5.15 eV. The solution energy for xenon at uranium vacancy sites is about 4.7 eV, slightly lower than that at tri-vacancy. This is different from shell model results which predicted that cation vacancy had a much lower solution energy than tri-vacancy. With LSDA+U calculations, though uranium vacancy has the lowest solution energy, the tri-vacancy is at a level of just 0.4 eV higher. In contrast, COT clusters are about 1.8 eV higher in solution energy, mainly due to the few concentration of COT-v trap in the incorporation process (a) and the great incorporation energy in the case (b).

When decrease the temperature to 700 K, because of the change in trap concentrations,
the solution energy of xenon at uranium vacancy sites reduces 0.7 eV, as shown in figure 7. This change is important since it almost excludes the possibility for xenon atoms to occupy tri-vacancy sites. The influence of oxygen clusters is also non-trivial here. At 700 K, inclusion of COT clusters increases the solution energy of xenon at uranium vacancy sites by a value of 0.5 eV to 4.5 eV. This effect takes 43% of the solution energy difference between xenon at uranium vacancy and at tri-vacancy sites, thus is significant. Furthermore, since concentration of oxygen defect clusters are inversely proportional to temperature, at lower temperatures this indirect influence will become more distinct.

For all trap sites that were investigated in this work, the solution energies are positive. It indicates the insolubility of xenon gas in bulk UO$_2$. But as a fission reaction product, xenon keeps in the fuel matrix until it diffuses to grain boundaries and forms large bubbles. Before that, gas atoms might distribute randomly in the material and grow into small bubbles at defect sites or on dislocation loops. The moderate solution energy difference of xenon between at uranium vacancy and at tri-vacancy sites in $x > 0$ regime suggests that one can change temperature to tune the incorporation behavior of xenon, and then the bubble growth rate. This provides an alternative point to investigate the fuel swelling mechanism and the consequent structure damage imposed to the fuel and/or the cladding.

V. COMPARISON WITH OTHER THEORETICAL CALCULATIONS

There were several DFT calculations on the incorporation behavior of xenon in UO$_2$ published recently. It is valuable to summarize these results and compare with our calculations. The results of DFT calculations and those computed using semi-empirical shell model potentials are listed in table II. These data are scattered, but a common trend is obvious. All calculations that conducted at different theoretical levels predicted that the lowest incorporation energy for xenon is at the tri-vacancy site, and the highest energy is at the octahedral interstitial site, which is then followed by the oxygen and the uranium vacancy sites. Only the GGA results of Ref. predicted a different order. Its Xe(U) has an incorporation energy as high as 13.9 eV. This might originate from size effect since they employed a small supercell containing only 12 atoms. In a recent GGA calculation using a larger supercell containing 96 atoms, this value was reduced to 6.04 eV and became qualitatively consistent with other calculations. In addition, there is a digital scattering with
TABLE II: Calculated incorporation energies of xenon in UO$_2$ at various trap sites by different methods: the uranium site (U), the oxygen site (O), the octahedral interstitial site (Int), the tri-vacancy site (tri-V) and the cuboctahedron site (COT).

| $E^i$ (eV) | COT-xe | Xe(Int.) | Xe(U) | Xe(O) | Xe(tri-V) |
|------------|--------|----------|-------|-------|-----------|
| LSDA+U$^a$ | 3.10   | 9.75     | 3.87  | 7.53  | 0.18      |
| GGA+U$^{11}$ | –      | 11.11    | 2.5   | 9.5   | 1.38      |
| GGA+U$^{12}$ | –      | 8.07     | 5.18  | 9.01  | 2.90      |
| GGA$^{11}$ | –      | 12.75    | 6.04  | 9.71  | 2.12      |
| GGA$^9$    | –      | 11.2     | 13.9  | 9.4   | –         |
| Shell model$^1$ | –      | 17.23    | 4.99  | 13.34 | 1.16      |
| Shell model$^2$ | –      | 18.67    | 5.83  | 15.15 | 3.3       |

$^a$ this work

A magnitude of 1~2 eV in these DFT results. This might be due to the different methodologies that were employed, for example the different exchange-correlation functionals, the constraints on structure optimization process, the effective Hubbard parameters, and so on. Meta-stable states might also play some role here.

The incorporation energies of xenon calculated by Nerikar et al.$^{11}$ are 1~2 eV higher than ours, except that at uranium vacancy where their value is about 1 eV smaller. As for the solution energies, they predicted the stability of xenon at tri-vacancy in the hypo-stoichiometric regime with a solution energy of 3.88 eV, about 2 eV smaller than ours. This is because though we have a similar binding energy for point defects to form a tri-vacancy, our formation energies of individual point defects are higher than theirs. In hyper-stoichiometric regime, they and we both predicted that uranium vacancy is the favored site for xenon at low temperatures. Again our value is about 2 eV higher. Without considering oxygen clustering and finite temperature effects, Nerikar et al. failed to notice the variation of the solution energy with temperature and the thermodynamic competition among tri-vacancy, uranium vacancy and other possible complex traps (e.g., di-vacancy), which we have shown are important for understanding the physical behavior of realistic nuclear fuels.
VI. CONCLUSION

With LSDA+$U$ calculations, the incorporation behavior of xenon atoms at various trap sites in UO$_2$ was analyzed by studying the electronic structure and energetics. In the regime of UO$_{2-x}$, the result was that the gas atom prefers to tri-vacancy sites, while in UO$_{2+x}$ uranium vacancies are favored. COT clusters have large enough space at their centers but are not occupied by xenon atom due to subtle electronic de-hybridization of O 2$p$ and U 5$f$ orbitals when xenon atom goes in and the central oxygen out. The calculated solution energies showed that a thermodynamic competition between Xe(U) and Xe(tri-V) is significant, and the indirect influence of oxygen clustering is important. At uranium vacancy site, xenon is ionized to Xe$^+$ state, confirmed early semi-empirical prediction. This kind of charge transfer indicates that xenon bubbles cannot initiate from uranium vacancies but neutral tri-vacancy sites. Thus one can tune the occupation probability of xenon at tri-vacancy sites and then the bubble growth rate by control temperature. A approach to solve the meta-stable states difficulty that frequently encountered in DFT+$U$ applications was proposed, which exploits the coupling between ionic and electronic sub-systems and uses a quasi-annealing procedure to relax the electronic system to the ground state. It was shown that this method can effectively avoid meta-stable states.

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The importance of oxygen clustering on thermodynamic behavior of UO$_2$ also manifests in facilitating oxygen diffusion by via V-3O$^{''}$ clusters, as discussed in D. A. Andersson et al., Phys. Rev. B 80, 060101(R) (2009). Though in equilibrium states this cluster has a low concentration (see Ref. [22]), they might present transiently as an intermediate state in the diffusion process of point oxygen interstitials.

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