Ab initio Calculations of Defect Energetics in UO$_2$ [*]

Younsuk Yun,a Hanchul Kim,b Kwangheon Park,a

a Department of Nuclear Engineering, Kyung-Hee University, Suwon, , 449-701, Korea.
b Korea Research Institute of Standard and Science, P.O.Box 102, Yuseong, Daejeon, 305-600 Korea.

1 Introduction

The behaviour of fission gases is an important parameter for the safety of nuclear fuel material. Vacancies are thought to be a major diffusion channel for fission gases in UO$_2$ [1]. It is important to understand the nature of defects to investigate the diffusion mechanism in nuclear reactors. Much theoretical research has been devoted studying the diffusion of fission gases through vacancies [2–5]. However, there have been some debates regarding the calculated results. Grimes *et al.* predicted that di-vacancy emits the lowest solution energy for xenon (Xe) and krypton (Kr) atoms in UO$_2$ using the Mott-Littleton approximation with empirical potentials [4]. Petit *et al* applied the density functional theory using the local density approximation (DFT-LDA) with a supercell containing 24 atoms, and suggested that tri-vacancy is the most stable solution site for Kr [5]. In this work, we applied the density functional theory using the generalized gradient approximation (DFT-GGA) method and took advantage of a 98-atom supercell. We calculated the solution energy of Xe at various vacancy sites, and determined the most stable positions of Xe. From the obtained results, we suggest that tri-vacancy is the most preferable accommodation site of Xe and the most important defect site affecting the diffusion process of fission gases in UO$_2$.

2. Calculational details

There are two common types of intrinsic defects in ionic crystals: Frenkel and Schottky defects. Frenkel defects are vacancy-interstitial pairs that are far apart and do not interact with each other. Formation energy of Frenkel pair in UO$_2$, E_{FP}^f, is given by,

$$E_{FP_i}^f = E_{V_i}^{N-1} + E_{I_i}^{N+1} - 2 \times E^N \qquad (1)$$

where E^N is the total energy of the perfect crystal containing N atoms, and $E_{V_i}^{N-1}$ and $E_{I_i}^{N+1}$ are the total energies of the system with the vacancy and the interstitial of i element, which is a U or O atom. Schottky defects are three disconnected defects of two oxygen vacancies and one uranium vacancy. Formation energy of the Schottky defect in UO$_2$ is defined as

$$E_{SP}^f = E_{V_U}^{N-1} + 2 \times E_{V_O}^{N-1} - 3 \times E^N - \mu_{UO_2} \qquad (2)$$

where μ_{UO_2} is the chemical potential of three atoms corresponding the Schottky trio pair.

Four kinds of point defects, which are uranium vacancy, oxygen vacancy, di-vacancy and tri-vacancy, are known trap sites of fission products in UO$_2$ [2–6]. In the previous work, Catlow and Grimes showed that the formation energies of a trap site are related to Frenkel and Schottky energies in terms of thermodynamics relations [4, 8]. The appropriate expressions in strictly stoichiometric composition are given in Table 1.

Table 1 Formation expression of Xe trap sites derived from Frenkel and Schottky energies.

Formation energy of trap site of Xe	Formation expression in UO$_2$
$E_{V_O}^f$ (eV)	$\dfrac{1}{2} E_{FP_O}^f$
$E_{V_U}^f$ (eV)	$E_{SP}^f - E_{FP_O}^f$
$E_{V_{di}}^f$ (eV)	$E_{SP}^f - \dfrac{1}{2} E_{FP_O}^f - E_{di-vac.}^b$
$E_{V_{tri}}^f$ (eV)	$E_{SP}^f - E_{tri-vac.}^b$

To determine the stability of fission products trapped at defect sites, the incorporation and solution energy can be defined as following [4],

$$E^C = \left\{ E^{Xe\ in\ V_E} - E^N \right\} - \left\{ E_{V_E}^{N-n} - E^N \right\} \qquad (3)$$

$$E^S = \left\{ E^C \right\} - \left\{ E_{V_i}^f \right\} \qquad (4)$$

where $E^{Xe\ in\ V_E}$ is the total energy of the system with Xe trapped at a pre-existing vacancy site, and E^c and E^s are the incorporation and solution energies of Xe. n is the number of vacancies, and $E_{V_i}^f$ is the trap site formation energy obtained by the thermodynamic relations as given in Table 1.

3. Results and Discussion

Figure 1(a) is a conventional unit cell of UO$_2$, and Figure 1(b) shows a 2×2×2 supercell including 32 primitive unit cells of UO$_2$ used in this work. The corners of the small cube in Figure 1(a) are the

sites of oxygen atoms, and the black circles on the outer cube indicate uranium atoms. There are 27 small cubes in the 2×2×2 supercell shown in Figure 1(b), and the centre of alternating small cubes are occupied by uranium atoms. Figures 1(c), (d), (e), and (f) show the four kinds of vacancies known as Xe trap sites. In this work, the energetics study is restricted to neutral defects. We assume that the energy differences among the different charged states of the defects should be negligible compared with the differences among the energies of different kind of defects [7].

●: uranium atom   ○: oxygen atom   □: uranium vacancy   ⊘: oxygen vacancy
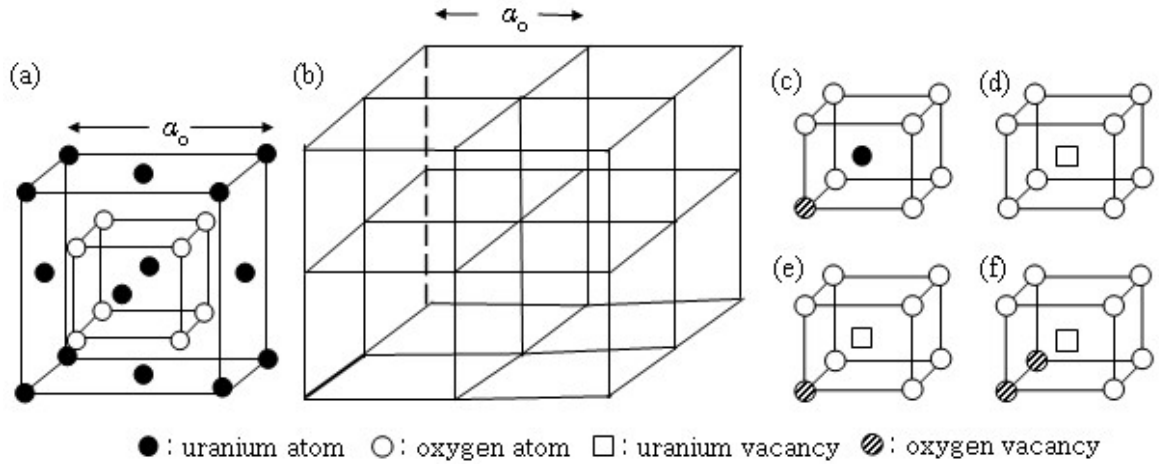
Figure 1 (a) Conventional unit cell of UO$_2$ containing 4 primitive unit cells, (b) A 98-atom supercell containing 32 primitive unit cells, (c) O vacancy, (d) U vacancy, (e) di-vacancy and (f) tri-vacancy. The lattice constant, α_0 , is 5.35 Å.

Table 2 Relative solution energy* of Xe.

Solution energy of Xe	Mott-Littleton	This work
$E^{s}_{v_O}$ (eV)	-0.48	-4.74
$E^{s}_{v_U}$ (eV)	-5.93	-10.10
$E^{s}_{v_{di}}$ (eV)	**-7.71**	-14.41
$E^{s}_{v_{tri}}$ (eV)	-7.66	**-17.12**

The solution energy for interstitial sites is shifted to be zero.

For the vacancy trap sites, the solution energies of Xe are summarized in Table 2. The present results are compared to the previous study, which used a different theoretical technique using empirical potential: the Mott-Littleton method. We should emphasize that the solution energies of trap sites are relative to that of interstitial sites, that is, the data shown in Table 2 are obtained as the energy for an interstitial site minus the energy for other trap sites. The bold numbers indicate the lowest solution energy.

In this work, the minimum solution energy is obtained when a xenon atom occupies a tri-vacancy. This discrepancy may be largely due to different binding energies of the vacancies. The binding energies of di-vacancy and tri-vacancy were

obtained to be 3.24 and 4.93 eV by Grimes' *et al* [4], and 0.39 and 0.51 eV, respectively, in this work. To gain further insight into the description for the solution energy, we examined the most stable positions of Xe among the considered embedded positions at each vacancy site, and the most stable positions which give the lowest total energy were at tri-vacancy sites.

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