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Atomic diffusion mechanism of Xe in UO_2

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ABSTRACT

We have investigated vacancy-assisted diffusion of Xe in uranium dioxide (UO_2) calculating incorporation, binding, and migration energies. All the energy values have been obtained using the density functional theory (DFT) within the generalized gradient approximation (GGA) and the projector-augmented-wave (PAW) method. Considering spin-polarization effect, we find that the computed migration energy is reduced by and agrees well with experimental data compared to those obtained from non-magnetic calculations. We also find that an oxygen vacancy lowers the migration energy of a uranium vacancy by about 1 eV, enhancing an effective movement of vacancy clusters consisting of both uranium and oxygen vacancies. Furthermore, the strain energy of Xe is large enough to contribute to the clustering of vacancies making it the driving force for the vacancy-assisted diffusion of Xe in UO_2. In summary all the calculated results suggest that the trivacancy is a major diffusion pathway of Xe in UO_2.

1. Introduction

The atomic transport processes in UO_2 are of great interest for understanding UO_2's performance during irradiation. Particularly, the behavior of fission gases is an important performance-limiting factor since fission gas release increases the temperature due to a decrease in the thermal conductivity across the fuel clad gap, resulting in an increase of the fuel pressure. For these reasons, the diffusion characteristics of fission gases have been the subject of extensive research [1–4]. Lawrence [5] has reviewed data on gas diffusion in UO_2 and reported that the diffusion coefficient of fission gases is significantly affected by the defect structure of UO_2. The detailed lattice structural analysis done by Matzke et al. [6–8] reports the fission gas diffusion in UO_2 at low gas concentrations to proceed via an electrically neutral trivacancy that consists of a uranium vacancy and two oxygen vacancies. Recently, experimental methods using *in situ* TEM (transmission electron microscope) experiments [9] and PIXE (particle induced X-ray emission) measurements [10] have been used to investigate the location and diffusion of fission products such as Xe, He, and Nd.

Several theoretical methods have also been used to study the behavior of fission products in UO_2. Catlow et al. [11,12] and Grimes et al. [13–15] calculated incorporation and solution energies of Xe and He in UO_2 using the Mott–Littleton approximation with empirical potentials. *Ab initio* methods based on the DFT [16] have been successfully used since the mid-90's. Petit et al. [17] investigated the stability of Kr in UO_2 applying the linear muffin–tin orbital method in the atomic sphere approximation [18,19], and Crocombette [20] also calculated the energies of Kr, I, Cs, Sr, and He in UO_2. Recently, Freyss et al. [21] compared the volume variation induced by He and Xe, by using the pseudopotential and the GGA method [22].

Despite the large amount of work performed, the mechanisms of fission gas release in UO_2 are still not known. One reason for this may be large variation in experimental data for the diffusion coefficient and activation energy which make it extremely difficult to develop constant plausible models based on experimental observations. In addition to this, most of the previous studies concentrated on the stability of fission products, rather than on diffusion mechanism.

In this study, we therefore focus on studying the atomic diffusion mechanism of Xe, which is one of the highest fractional released fission gases in UO_2. The GGA-PAW method [23] is used to obtain energy values. In particular, we focus on the role of point defect, especially vacancy defects, which is thought to be a major diffusion channel for fission gases in the UO_2 matrix [7,15,17]. A larger supercell containing 96 atoms is employed to reduce any artificial error caused due to the use of a small supercell. First, we calculate the incorporation energy [15,20,21] of Xe located at different five vacancies. These are the uranium vacancy (V_U), oxygen vacancy (V_O), divacancy consisting of a uranium and an oxygen vacancy (V_{UO}), trivacancy (V_{UO_2}), and tetravacancy ($V_{U_2O_2}$). The stability of these vacancies as Xe sites are compared using the relative incorporation energies. Next, we calculate the movement of defect

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elements and investigate the effect of the spin-polarization on the computed migration energies. Finally, we examine the diffusion mechanism of Xe with the effective movements of vacancies and predict a detailed diffusion process of Xe by a vacancy-assisted mechanism in the UO_2 lattice.

2. Calculation details

Fig. 1(a) and (b) show unitcell and a $2 \times 2 \times 2$ supercell of UO_2, respectively. The energy needed to incorporate a free Xe atom at an octahedral interstitial site (OIS) in UO_2 is calculated as shown

$$E^{I}_{Xe_{OIS}} = E^{N+1}_{Xe_{OIS}} - (E^{N}_{perfect} + E_{Xe_{free}}) \quad (1)$$

where $E^{N+1}_{Xe_{OIS}}$ is the total energy of a supercell containing Xe trapped at an OIS, and $E^{N}_{perfect}$ is the energy of a defect-free supercell. $E_{Xe_{free}}$ is the energy of free Xe atom and N is the number of atoms in a supercell. In this study, focus is on the relative incorporation energy of Xe between an OIS and other trap sites assuming that Xe exists in UO_2. We calculate the relative incorporation energies of Xe for five different trap sites: V_O, V_U, V_{UO}, V_{UO_2}, and $V_{U_2O_2}$ shown in Table 1.

Fig. 2 describes the details of calculating the relative incorporation energy. The system S_1 in Fig. 2 indicates two structures containing Xe_{OIS} and a V_Z which is a vacancy of the Z-element (Z= cation, anion, or their compounds), respectively. These two structures are far enough from each other to ignore the interaction between Xe_{OIS} and V_Z. S_2 consists of a perfect crystal and a Xe_Z-containing system.

The relative incorporation energy of Xe for an OIS and V_Z is calculated from the total energy difference between the S_1 and S_2 as follows:

$$E_I = E_{S_2} - E_{S_1} = (E^{N}_{perfect} + E^{N}_{Xe_Z}) - (E^{N+1}_{Xe_{OIS}} + E^{N-1}_{V_Z}) \quad (2)$$

We calculated the formation energies of the oxygen Frenkel pair and Schottky defects, respectively, as follows. These are known as the dominant intrinsic defects in UO_2

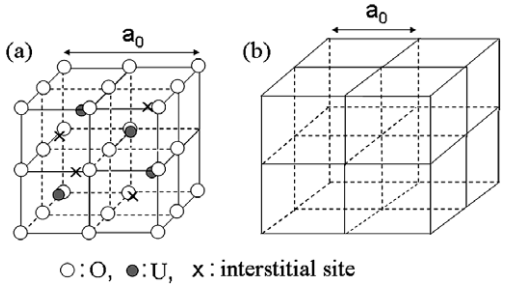

Fig. 1. (a) Conventional unitcell of UO_2. Oxygen atoms are located at the corners of small cubes, and uranium atoms are located at the center of an alternative cubes. × indicates the octahedral interstitial site in FCC structure. (b) A $2 \times 2 \times 2$ supercell of UO_2 containing 96 atoms used in the current study.

Table 1
Calculated incorporation energies of Xe for five different vacancies and OIS

Xe sites	OIS	V_O	V_U	V_{UO}	V_{UO_2}	$V_{U_2O_2}$
Incorporation energy (E^I) (eV)	1.43	−2.90	−6.83	−9.71	−10.97	−12.07
Formation energy (E^f_V) (eV)	0.00	1.84	3.27	4.71	6.44	8.13
$E^I + E^f_V$	1.43	−1.06	−3.56	−5.00	−4.52	−3.94

$E^f_{F_O} = 3.7(3.0\text{–}4.0)^*$, $E^f_S = 7.0(6.0\text{–}7.0)^*$.
The incorporation energy is increased as the size of vacancy. The formation energy of each vacancy is derived by using the thermodynamic relation between oxygen Frenkel pair and Schottky defects [13–15]. (* indicates the experimental data of the formation energies of oxygen Frenkel pair ($E^f_{F_O}$) and Schottky trio (E^f_S) defects [34]).

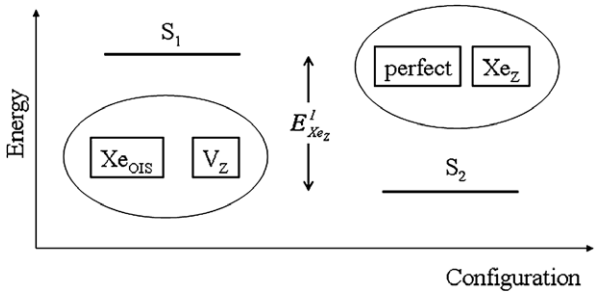

Fig. 2. Incorporation energy of Xe at a vacancy. The system S_1 contains Xe_{OIS} and V_Z: Xe is located at OIS and V_Z is a vacancy of Z-element which is uranium atom, oxygen atom, or their compounds. The S_2 contains Xe_Z that Xe trapped at V_Z. The incorporation energy of Xe for V_Z, $E^I_{Xe_Z}$, is calulated the energy difference between the S_1 and S_2.

$$E^f_{F_O} = E^{N-1}_{V_O} + E^{N+1}_{I_O} - 2 \times E^N \quad (3)$$

$$E^f_S = E^{N-1}_{V_U} + 2 \times E^{N-1}_{V_O} - 3 \times E^N + \mu_U + 2 \times \mu_O \quad (4)$$

$$= E^{N-1}_{V_U} + 2 \times E^{N-1}_{V_O} - 3 \times E^N + \mu_{UO_2} \quad (5)$$

μ_U and μ_O indicate the chemical potentials of U and O atoms, respectively. The U and O chemical potentials are related at equilibrium by

$$\mu_U + 2\mu_O = \mu_{UO_2} \quad (6)$$

where μ_{UO_2} is obtained from the cohesive energy per UO_2 unitcell [24,25]. Using the thermodynamic relation between oxygen Frenkel and Schottky defects, the formation energies of the vacancies considered as trap sites in UO_2 are derived as shown [13–15]

$$E^f_{V_O} = \frac{1}{2} E^f_{F_O} \quad (7)$$

$$E^f_{V_U} = E^f_S - E^f_{F_O} \quad (8)$$

$$E^f_{V_{UO}} = E^f_S - \frac{1}{2} E^f_{F_O} - E^b_{V_{UO}} \quad (9)$$

$$E^f_{V_{UO_2}} = E^f_S - E^b_{V_{UO_2}} \quad (10)$$

We apply to these relations to the formation energy of $V_{U_2O_2}$ as shown below:

$$E^f_{V_{UO_2}} = E^f_S + \frac{1}{2} E^f_{F_O} - E^b_{V_{U_2O_2}} \quad (11)$$

The movement of vacancies and Xe is investigated by calculating their migration energies. The corresponding energy barrier is obtained at saddle points in their diffusion pathways (See Fig. 3). All the energy values were obtained using the VASP code [26–28]. The PAW method is employed to describe the electron-ion interaction. For the exchange and correlation energy of electrons, we have adopted the conventional GGA approach, because first-principles calculations to the GGA approximation showed that it can give almost correct energy information for UO_2, regardless of the fact that a wrong electronic band structure was predicted [29–32]. Plane waves with a kinetic energy up to 500 eV were used to expand the wave functions, and the electron charge density was obtained by using a $2 \times 2 \times 2$ k-point grid within the Brillouin zone. For all the defect structures, ionic relaxation was performed, and the force acting on each ion was calculated until less than 0.01 eV/Å. Meanwhile, it should be noted that the energy calculations were done by assuming 0 K in this study, even though the movement of point defects can occur at least over 500–600 °C in UO_2. A thermal vibration of the lattice atoms can increase the total energy of a system by about 0.1 eV on average when the system temperature is raised to 1000 °C. However, in this study, the energy value of 0.1 eV could be considered an acceptable error, because the energy change