A study on defect energy in UO_2 lattice using ab initio DFT

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1. Introduction

The behavior of fission gases is an important limiting factor for the nuclear fuel performance, as fission gas release affects the pressure and temperature of the fuel rod [1]. The point defects are a major diffusion channel for fission gases. The defect energies and mobility energies are needed to know the fission gas mobility in point defect.

In this study, we performed ab initio total energy calculations to investigate the defect energies and employed a large super cell containing 96 atoms to decrease defect-defect interaction. The formation energy of intrinsic defects indicates that the accuracy of the present modeling is significantly improved, compared with previous studies.

2. Calculation details and Results

2.1 Ab initio methods.

Electronic structure calculations by ab initio techniques enable determining quantities inaccessible to experiments because of either too small a length of scale or the impossibility to isolate the contribution of a given factor on the studied physical properties. In particular, ab initio calculations allow to study separately different types of point defects in a solid and to determine for each of them its stability (formation energy) or its influence on the crystal structure (atom relaxation around the defect, swelling of the crystal). These data can then be used as input in thermodynamical models at a macroscopic scale [2].

In the study, we calculated the total energies using the VASP code. 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.

2.2 Parameter calculating in Unit cell.

Three parameters (*k*-point, energy cut-off and lattice constant) are very important factors to obtain the total convergence energies for UO_2. We calculated to obtain the total convergence energies as *k*-point, energy cut-off, and lattice constant for UO_2 unit cell using the ab initio DFT method.

As we obtained a metallic state we had to use a sampling grid of the Brillouin zone that contains many *k*-points. The convergence with the number of k points (generated following the Monkhorst and Pack scheme) is given in Fig. 1.
Fig.1 shows the total energy converging with increasing number of *k*-points.

The convergence of the total energy of the UO_2 unit cell with the energy cut-off is given in Fig. 2. Total energy is converged into a stable value with an increase in the cut-off energy.

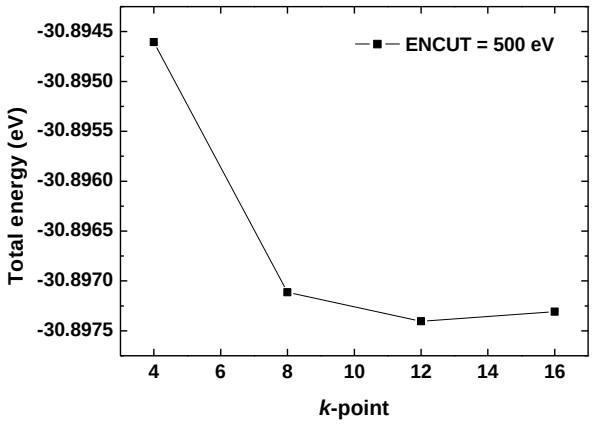

Fig.1 Convergence of the total energy *E* per structural unit as a function of the number of *k*-points for UO_2 fluorite structure.

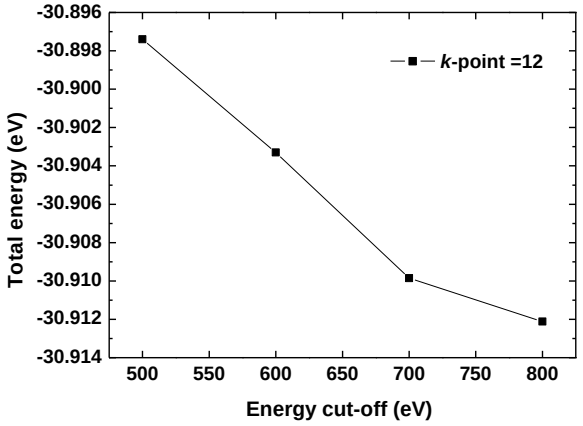

Fig.2 Convergence of the total energy *E* per structural unit as a function of energy cut-off for UO_2 fluorite structure.

Lattice constant was implied in [3]. This value is about 5.44 Å.

2.3 Calculating in Super cell

The PAW method is employed to describe the electron-ion interaction. For the exchange and correlation energy of electrons, we have adopted a conventional GGA approach, because first-principle 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. Plane waves with a kinetic energy of up to 550 eV were used to expand the wave functions, and the electron charge density was obtained by using a $2\times2\times2$ 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/A.

The free energy of formation of a point defect is defined as the free energy difference between the system with and without the defect,

$$F^F = E^F - TS^F$$

where E_F and S_F are, respectively, the variation of internal energy and entropy associated with the creation of the defect. Internal energy of formation for each defect can be easily calculated from the energies of the cell: for the Frenkel pairs,

$$E_{F_O}^f = E_{V_O}^{N-1} + E_{I_O}^{N+1} - 2\times E^N$$

for the Schottky defect,

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

E^N is the calculated energy of the defect free cell; $E_{PD}^{N\mp1}$ is the calculated energy of the cell with the point defect; N denotes the number of atoms in the defect free cell (96 in the present case). The entropy of formation is the variation of vibrational entropy between the defect free and defective crystal. To obtain the exact value of this term, phonon distributions of the perfect and defective cells should be calculated [4].

Table 1 show the calculated results and compares them with the experimental and previous theoretical results.

Table 1 Formation energies of intrinsic point defects in UO_2 (eV).

	Oxygen Frenkel pair	*Schottky defect*
Exp.	3.0-4.6	6.0-7.0
Mott-Littleton	6.8	13.3
LDA-PP(24-atom cell)	3.9	5.8
GGA-PAW(96-atom cell)	3.7	7.0
This work(96-atom cell)	3.5	4.9

Using the thermodynamic relation between oxygen Frenkel and Schottky defects, the formation energies of the vacancies considered as trap sites in UO2 are derived as shown in [5].

$$E_{V_O}^f = \frac{1}{2}E_{F_O}^f$$

$$E_{V_U}^f = E_S^f - E_{F_O}^f$$

$$E_{V_{UO}}^f = E_S^f - \frac{1}{2}E_{F_O}^f - E_{V_{UO}}^b$$

$$E_{V_{UO_2}}^f = E_S^f - E_{V_{UO_2}}^b$$

Table 2 calculated results for formation energies of extrinsic point defects in UO_2.

Table 2 Formation energies of extrinsic point defects in UO_2

Formation energy(E_V^f) (eV)	V_O	V_U	V_{UO}	V_{UO_2}
This work	1.75	1.44	2.70	4.20
GGA-PAW [1]	1.84	3.27	4.71	6.44

4. Conclusions

To observe the parameter information given the optimum value, we calculated the convergence total energy using the ab initio method in the unit cell, and based on this, obtained the point defect formation energies in UO_2 lattice super cell.

First, we obtained the value in table 1 for the formation energies of intrinsic point defects in UO_2. The present results agree with experimental data and the LDA-PP calculations by Crocombette et al [4]. In table 1, the Schottky formation energy obtained by experiment and the Mott-Littleton method [5] are almost twice as large as the Frenkel formation energy. The defect formation energy by the Mott-Littleton method tends to be overestimated more than the experimental data and ab initio calculations.

Second, we investigated the formation energies of extrinsic point defects in UO_2. The reason for the difference in the results is because we calculated the Schottky formation energy using a solution by Crocombette, but other values calculated Schottky formation energy using a solution for the chemical potential of UO_2.

This study will be helpful to research defect energy properties for nuclear fuels.

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