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

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1. Introduction

Several advanced nuclear fuels, with significantly improved properties compared to the current commercial oxide fuels, are being investigated in the context of Generation-IV reactors. Uranium nitride is in particular generating a lot of interest owing to its superior thermophysical properties such as high thermal conductivity and high metal density [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 64 atoms to decrease the defect-defect interactions. We calculated the formation energy and incorporation of UN defects, and analyzed the results.

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 thermo dynamical models at a macroscopic scale [2].

In the study, we calculated the total energies using the VASP.4.6 code. All the energy values were 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, cut-off energy, and lattice constant) are very important factors to obtain the total convergence energies for UN. We calculated the total convergence energies as *k*-point, cut-off energy, and lattice constant for UN 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. The convergence of the total energy of the UN unit cell with the cut-off energy is given in Fig. 1.

Total energy is converged into a stable value with an increase in the number of *k*-points and the cut-off energy.

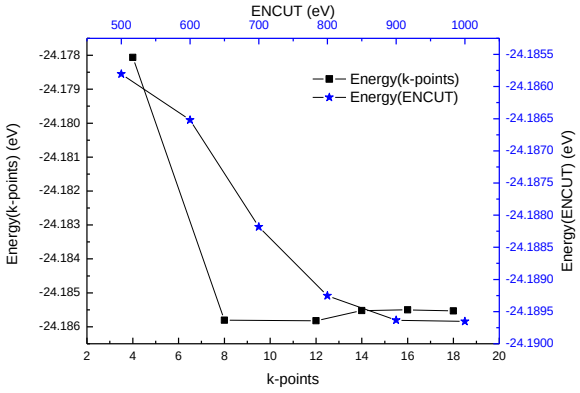

Fig. 1 Convergence of the total energy *E* per structural unit as a function of the number of *k*-points and the cut-off energy for a UN rock-salt crystal structure.

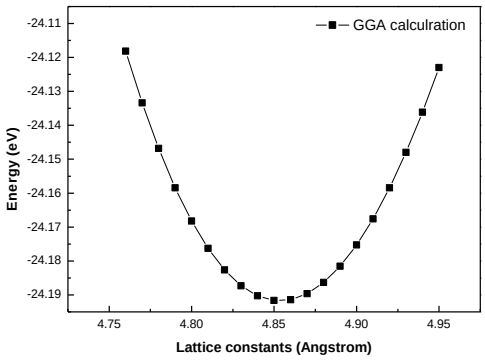

Fig. 2 The dependence of total energy on the lattice constant.

The lattice constant was contained to using stable values with k-points and the cut-off energy. The

calculated equilibrium lattice constant was about 4.85 Å, which is underestimated by about 0.8% compared with the experimental value of 4.89 Å [3].

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 UN, regardless of the fact that a wrong electronic band structure was predicted. Plane waves with a kinetic energy of up to 500 eV were used to expand the wave a functions. The Monkhorst-Pack k-point scheme of $4\times4\times4$ mesh was employed for the 64-atom supercell. 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.

2.3.1 Formation energies

The formation energy of a vacancy E_F^X is calculated from the following expression:

$$E_F^X = E_{UN*} - E_{UN} + E_{UorN}.$$

while the Schottky defect formation energy E_F^{SD} is expressed as follows:

$$E_F^{SD} = E_{UN**} - E_{UN} + E_U + E_N.$$

E_{UN*} and E_{UN**} are the energies of the supercell containing one vacancy (at the N or U site) and Schottky defects (along the [100] or the [111] direction), respectively, E_{UN} is the energy of the perfect UN 64-atoms supercell, and E_{UorN} is the energy per atom of the missing element (uranium or nitrogen) in its ground state. It should be pointed out that the values for defect formation energies are somewhat arbitrary due to the fact that they depend on reference energies for E_{UorN}, and there is more than one choice for the reference state.

In this study, we chose some reference energy for E_{UorN} in order to compare it with that one from other work [1,4]. The reference energy E_{UorN} is N= -3.12 eV and U= -4.09 eV.

Table Ⅰ shows the calculated results and compares them with previous theoretical results.

Table Ⅰ Formation energies for point defects at N and U sites, and Schottky defects along the [100] and [111] direction.

	N site	U site	[100]	[111]
This work	11.88	10.16	21.26	21.89
Ref.[1]	9,43	10.55	19.34	19.86

2.3.2 Incorporation energies

Defect energetics can be characterized by the incorporation, relaxation, and solution energies, as demonstrated by Grimes and Catlow [4] for fission products in uranium dioxide. The incorporation energy $E_{Inc.}$ is calculated according to

$$E_{Inc.} = E_{UN}^{Xe} - (E_{UN*} + E_{Xe}).$$

The incorporation energy $E_{Inc.}$ is defined as the energy required to incorporate an atom at a pre-existing vacancy or interstitial site. E_{UN}^{Xe} is the energy of the supercell containing the fission product, E_{UN*} of the supercell with the vacant host site are for the interstitial incorporation, this energy corresponds to E_{UN} and E_{Xe} corresponds to the energy of an isolated atom of Xe.

Tables Ⅱ shows the calculated results. The incorporation energies in the Schottky defects were calculated to atoms site each.

Table Ⅱ Incorporation energies of Xe for U site, N site, and interstitial sites, and Schottky defects in [100] and [111] Miller indices lattice planes.

	Middle	*N-site*	*U-site*
N	9.13		
U	4.84		
Interstitial.	15.04		
[100]	3.51	3.51	3.51
[111]	4.99	9.11	4.99

3. Conclusions

To observe the parameter information given the optimum value, we calculated the convergence of total energy using the ab initio method in the unit cell, and based on this, obtained the point defect formation energies in the UN lattice super cell. To find stable site on xenon, we calculated the incorporation energies of xenon for various defects.

Through this calculation, we obtained the formation energies and saw different values at each site. The reason for the difference in the results at the same formation is because we used a reference that differs from other work.

The incorporation energies of xenon revealed a clear preference for the larger sites available at uranium vacancies. The incorporation of xenon in Schottky defects was found to be more favorable at single vacancies. In particular, incorporation at the Schottky defects along the [100] direction was the most stable in this study.

This study will be helpful to research the defect energy properties and understand the acting fission products in nuclear fuels.

REFERENCES

[1] M. Klipfel, P. Van Uffelen, J. Nucl. Mater 422 (2012) 137-142.
[2] M. Freyss, T. Petit, J.P. Crocombette, J. Nucl. Mater 347 (2005) 44-51.
[3] Matzke Hj, Science of Advanced LMFBR Fuels (1986) (Amsterdam: North-Holland)
[4] R.W. Grimes, C.R.A. Catlow, phil. Trans. Roy. Soc. A 335 (1991) 609-634