First-principles study of helium clustering at initial stage in ThO_2*

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The clustering behavior of helium atoms in thorium dioxide has been investigated by first-principles calculations. The results show that He atoms tend to form a cluster around an octahedral interstitial site (OIS). As the concentration of He atoms in ThO_2 increases, the strain induced by the He atoms increases and the octahedral interstitial site is not large enough to accommodate a large cluster, such as a He hexamer. We considered three different Schottky defect (SD) configurations (SD_1, SD_2, and SD_3). When He atoms are located in the SD sites, the strain induced by the He atoms is released and the incorporation and binding energies decrease. The He trimer is the most stable cluster in SD_1. Large He clusters, such as a He hexamer, are also stable in the SDs.

Keywords: first-principles study, thorium dioxide, helium cluster, defective properties

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1. Introduction

Thorium dioxide is a robust nuclear fuel candidate for generation IV reactors because of its low generation of minor actinides, excellent radiation resistance and chemical stability.[1–4] During the reactor operation, production of noble gases may affect the mechanical and thermal properties of nuclear fuels.[5,6] One of these noble gases is helium, and most of the helium is generated by alpha decay during fuel burn-up. Because of its high diffusivity, helium tends to cluster and form bubbles, resulting in swelling of nuclear fuels.[7–9] Therefore, it is necessary to investigate the clustering behavior of helium in nuclear fuels.

Considering the difficulties in nuclear fuel experiments, effective theoretical calculations should be performed. Density functional theory (DFT) is a reliable method to evaluate the point defect energies by atomic-scale calculation.[10–13] In recent years, a number of computational works concerned with the bulk and defect properties of nuclear fuels have been performed.[14–21] Zhang *et al.*[14,15] investigated the mechanical and thermal properties of ThO_2 by first-principles calculations. Thompson *et al.*[16] reported that the stability of noble gas atoms is related to the strain they caused in trap sites. Ma *et al.*[17] studied the swelling of UO_2 induced by noble gases based on hybrid DFT. Brillant *et al.*[18] studied the stability and solubility of fission products, including helium, using spin-polarized generalized gradient approximation with on-site Coulomb correction techniques. Yun *et al.*[19] investigated the clustering behavior of He in UO_2, and found that He clusters affect the local mechanical properties of UO_2. Dabrowski *et al.*[20] reported that diffusion of helium between two octahedral sites in UO_2 is along a polyline rather than a straight line.

In the present work, we investigate the clustering behavior of helium by choosing an octahedral interstitial site (OIS) and the Schottky defect (SD) as the trap sites. The volume change of ThO_2 and incorporation and solution energies are then calculated with increasing concentration of He atoms. Finally, the stability of He clusters is discussed from the perspective of their calculated binding energies.

2. Methodology

Our calculations were performed using the density functional theory as implemented in the Vienna *ab initio* simulation package (VASP).[22,23] The projected augmented wave method (PAW)[24] and the generalized gradient approximation (GGA)[25] were used. The exchange and correlation energies were calculated using the Perdew–Burke–Ernzerhof (PBE) functional.[26] The wave functions were expanded in a plane-wave basis set with an energy cutoff of 500 eV. Since ThO_2 is a diamagnetic material,[14] the spin polarization was not considered in the calculation. The results were also checked with spin polarized calculations, which showed no obvious differences. Due to no inclusion of occupied 5f states, the strong correlation effect of ThO_2 was negligible. It

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has been reported[15,27] that the GGA approximation can give nearly correct energy information for ThO_2, and therefore the GGA+U method[28,29] was not adopted in this work. The lattice constants and internal freedom of the unit cell were fully optimized until the Hellman–Feynman forces on the atoms were less than 0.01 eV/Å. The effective charge for each atom was calculated using Bader charge analysis.[30]

In order to simulate the helium clusters incorporated in ThO_2, a 2×2×2 supercell containing 96 atoms was used in the calculation. The previous results[27,28] have proven that a supercell of this size can make the energies sufficiently converged. Depending on the unit cell size and shape, a 2×2×2 Monkhorst–Pack sampling mesh[31] of k-points was used. We implemented a k-mesh test for the He–ThO_2 system. The incorporation energy of He (discussed in the next section) calculated by 2×2×2 and 3×3×3 k-meshes has a little difference within the range of meV. This indicated that a 2×2×2 k-mesh is sufficient to avoid significant numerical errors in our calculations. All these calculations were checked using larger energy cutoffs and k-meshes; the results of total energy and Hellmann–Feynman forces were converged within 0.01 eV and 0.01 eV/Å, respectively. According to the previous work,[32–34] the zero point energy (ZPE) of helium in oxides is small, which does not affect the numerical results. This can be seen in some previous studies of similar material systems. For instance, when helium interacts with O atoms in Al_2O_3, ZPE corrections are in a range of 10^{-2}–10^{-3} eV.[32] Therefore, calculations without ZPE correction were employed in this work.

Table 1. Incorporation energy of He in octahedral interstitial site for different k-meshes.

k-mesh	Incorporation energy/eV
2×2×2	0.748
3×3×3	0.746
4×4×4	0.746

3. Results and discussion

ThO_2 crystallizes in a cubic fluorite structure (space group: $Fm3m$). Our calculated lattice constant is 5.617 Å, which agrees with the theoretical result (5.619 Å) reported by Zhang *et al.*[14] and the experimental value (5.597 Å) reported by Olsen *et al.*[35] To investigate the clustering behavior of helium in ThO_2, the following trap sites are considered: the octahedral interstitial site (OIS) and the Schottky defect (SD) as shown in Fig. 1. The SD clusters can be made by removing one thorium atom and two neighboring oxygen atoms from the lattice.[36] Thus three configurations of the Schottky defect (SD_1, SD_2, SD_3) can be considered, differing by the distance between the two oxygen vacancies.

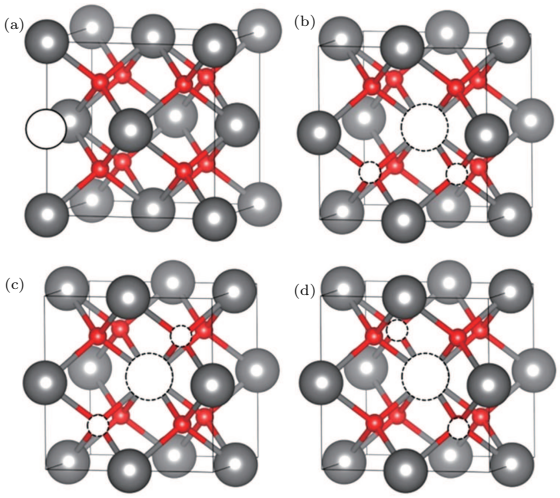


Fig. 1. (color online) (a) The cubic fluorite structure of ThO_2. The gray and red spheres represent the thorium and oxygen atoms, respectively. The solid spheres represent the OIS. (b) Three configurations of the Schottky defect: (b) SD_1, (c) SD_2, and (d) SD_3. The dashed spheres represent the vacancies.

It is known that helium atoms prefer to reside in octahedral interstitial sites in the perfect fuel matrix.[37] He atoms spontaneously move to OISs after atomic relaxation from their initial positions in other interstitial sites. The diffusion barrier plays an important role in the clustering process of He. We calculated the migration energy of He by the nudged elastic band (NEB) method.[38] The migration energy of He between two OISs is 3.80 eV, which is in agreement with the results reported by Dąrowski *et al.*[39] Considering the environment with a high temperature in nuclear fuels, we suggest that He tends to be mobile in ThO_2. In this work, we considered the clustering behavior of He atoms around an OIS with increasing concentration of He atoms. Firstly, we positioned two He atoms at the center of the edge between two oxygen atoms (Fig. 2), which is the midpoint between two interstitial sites. After relaxation, they both move to the center of an OIS and form a He dimer, as shown in Fig. 2(a).

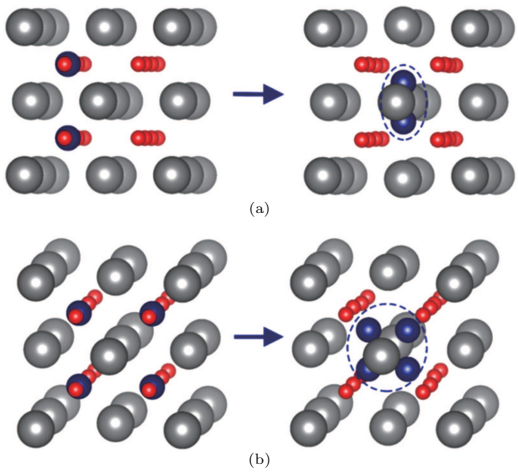


Fig. 2. (color online) The initial configurations of (a) two and (b) four He atoms and their configurations after atomic relaxation. The gray, red, and blue spheres represent the thorium, oxygen, and helium atoms, respectively.

The clustering behavior was investigated by increasing the concentration of He atoms in ThO_2. For four He atoms, a tetramer forms in an OIS, as shown in Fig. 2(b). For six He atoms, the He atoms do not form a hexamer, which we might except, but they form three dimers trapped in different OISs (see Fig. 3). This indicates that the OIS in ThO_2 does not have sufficient space to accommodate a large cluster, such as a hexamer. This result is different from the case in UO_2, where six He atoms tend to form a hexamer in the OIS and greatly displace the surrounding atoms.[19] The largest displacement of the surrounding oxygen atoms in our work is 0.23 Å (see Table 1), while the displacement of oxygen atoms can be as large as 0.65 Å in UO_2. We suggest that the oxygen and thorium atoms in ThO_2 are less mobile than the uranium and oxygen atoms in UO_2.

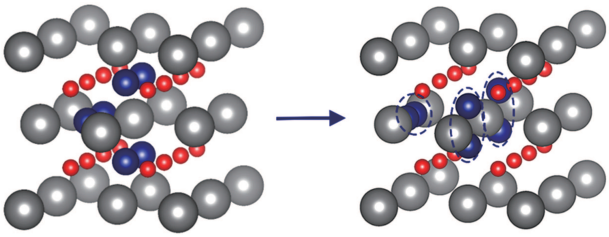


Fig. 3. (color online) The initial configurations of six He atoms and the configuration after atomic relaxation. Three dimers form in different OISs.

When He atoms are introduced into the supercell structure, the volume of the structure changes according to the doping site and the number of He atoms. This volume change is given by

$$\Delta V = V_{\mathrm{He}}^{X} - V, \tag{1}$$

where V_{He}^{X} is the volume of the supercell with a He atom trapped in defect X and V is the volume of the perfect supercell. The volume changes induced by the defects are listed in Table 2. There is almost no volume change for the incorporation of one He interstitial. When the number of He atoms increases, the volume of the supercell increases. For a He dimer, the volume variation slightly increases ($\Delta V/V = 0.4\%$). A He tetramer induces the largest swelling of the supercell ($\Delta V/V = 1.7\%$). Compared with four He interstitials, the volume change induced by six He interstitials is smaller. This indicates that the swelling induced by He atoms mainly depends on the size of the He cluster. As the size of the He cluster increases, the swelling of the supercell dramatically increases.

Table 2. Volume changes relative to the perfect supercell $\Delta V/V$, displacement of the nearest-neighbouring atoms of He Δd, incorporation energies E^{Inc}, and binding energies E^{B} with the increasing number of He atoms.

Number of He	$(\Delta V/V)/\%$	Δd/Å	E^{Inc}/eV	E^{B}/eV
1	0.1	0.02	0.75	–
2	0.4	0.08	3.43	1.93
3	0.9	0.18	6.12	3.87
4	1.7	0.23	10.64	7.64
6	1.4	0.11	10.26	–

To investigate the stability of the He clusters in ThO_2, we calculated the incorporation energies of He interstitials. The incorporation energy $E_{\mathrm{He}-X}^{\mathrm{Inc}}$ is defined as the energy required to incorporate a He atom in a pre-existing defect site,

$$E_{\mathrm{He}-X}^{\mathrm{Inc}} = E_{\mathrm{He}}^{X} - E^{X} - E_{\mathrm{He}}, \tag{2}$$

where E_{He}^{X} and E^{X} are the total energies of the system with and without incorporation of a He atom in trap site X, respectively, and E_{He} is the total energy of an isolated He atom. The calculated incorporation energies are listed in Table 2. The incorporation energy significantly increases with increasing number of He atoms in the ThO_2 supercell. Incorporation of a He tetramer requires the largest energy (10.64 eV). The incorporation energy of six He atoms slightly decreases because of the formation of smaller clusters. The binding energy of a He cluster was calculated as follows:

$$E^{\mathrm{B}} = E_{N\cdot\mathrm{He}\in X}^{\mathrm{Inc}} - N \times E_{\mathrm{He}\in X}^{\mathrm{Inc}}, \tag{3}$$

where N is the number of He atoms and $E_{N\cdot\mathrm{He}\in X}^{\mathrm{Inc}}$ is the incorporation energy of the He cluster in defect X. As shown in Table 2, all of the binding energies are positive, suggesting that binding of these He clusters in an OIS is an endothermic process. The binding energy increases with the size of the He cluster, and the tetramer has the largest binding energy of 7.64 eV. This indicates that a large energy barrier needs to be overcome when four He atoms migrate from isolated OISs to form a cluster in one OIS of ThO_2. The He dimer is the most stable cluster in the OIS with a binding energy of 1.93 eV.

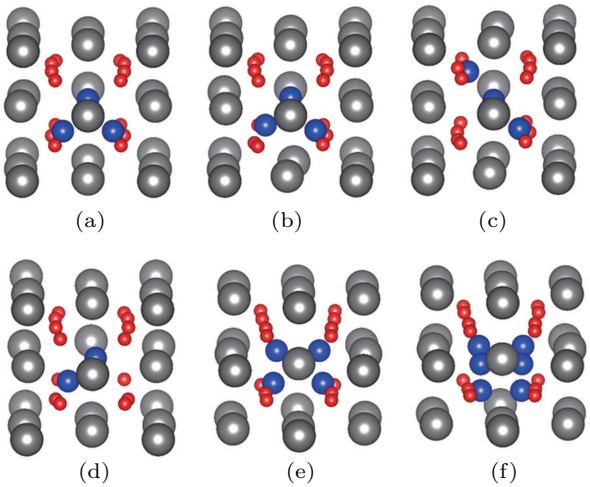


Fig. 4. (color online) The configurations of He trimmers in (a) SD_1, (b) SD_2, (c) SD_3; and (d) a He dimer, (e) a He tetramer, and (f) a He hexamer in SD_1.

The incorporation energy of He atoms is related to the strain.[16] Owing to the large strain induced by large clusters, an OIS does not seem to be the energetically favorable trap site for He atoms. Thus, we also considered the Schottky defect (SD) as the trap site, which can provide more empty space for

strain release. As shown in Fig. 4, three configurations of the Schottky defect (SD_1, SD_2, and SD_3) were considered, which differ by the distance between the two oxygen vacancies. He atoms tend to aggregate in the SDs after atomic relaxation, and even a He hexamer can exist in ThO_2 (see Fig. 4). The calculated $\Delta V/V$ and $E^{\rm Inc}$ of He clusters trapped in the SDs are listed in Table 3. As the concentration of He atoms in ThO_2 increases, both $\Delta V/V$ and $E^{\rm Inc}$ increase. A He hexamer in SD_1 has the largest incorporation energy of 3.35 eV, which also results in the largest volume change of 1.31%. As shown in Fig. 5, the incorporation energies of He atoms in the SDs are significantly smaller than those in OISs, suggesting that He clusters prefer to reside in SDs. The volume changes induced by He atoms in the SDs are also smaller than those in OISs. This indicates that these SDs are favorable for the release of the strain induced by incorporation of He clusters in ThO_2, especially for large clusters.

Table 3. Volume changes $\Delta V/V$ (in %) and incorporation energies $E^{\rm Inc}$ (in eV) of He clusters trapped in SDs with the increasing number of He atoms.

Number of He	SD_1		SD_2		SD_3	
	$\Delta V/V$	$E^{\rm Inc}$	$\Delta V/V$	$E^{\rm Inc}$	$\Delta V/V$	$E^{\rm Inc}$
1	0.39	0.01	0.42	0.03	0.30	0.20
2	0.50	0.34	0.48	0.33	0.36	0.32
3	0.56	0.57	0.55	0.62	0.40	0.66
4	0.84	1.53	0.88	1.64	0.75	1.67
6	1.31	3.35	1.16	2.67	0.88	2.41

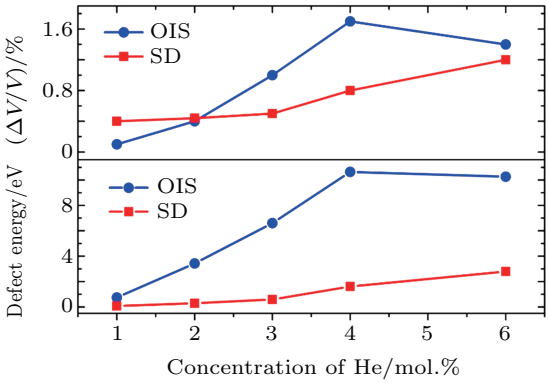


Fig. 5. (color online) The average volume changes $\Delta V/V$ and incorporation energies $E^{\rm Inc}$ of He clusters trapped in SDs, with comparison to those in an OIS.

Considering the energy cost for formation of the SD, we also calculated the solution energy

$$E^{\rm Sol}_{{\rm He}\in{\rm SD}} = E^{\rm Inc}_{{\rm He}\in{\rm SD}} + E^{\rm Fapp}_{\rm SD}, \quad (4)$$

where $E^{\rm Inc}_{{\rm He}\in{\rm SD}}$ is the incorporation energy of He atoms trapped in a SD and $E^{\rm Fapp}_{\rm SD}$ is the apparent formation energy of the SD. The apparent formation energies can be obtained by the point defect model proposed by Matzke[40] and Lidiard.[41] The calculated $E^{\rm Fapp}_{\rm SD}$ of SD_1, SD_2, and SD_3 are 4.84 eV, 4.25 eV, and 4.41 eV, respectively. The solution energies of He clusters in the SDs are given in Table 4 and Fig. 6. The solution energies in SD_1 are clearly larger than those in the other configurations. Most of the He clusters are more soluble in SD_2, while a He hexamer prefers to reside in SD_3.

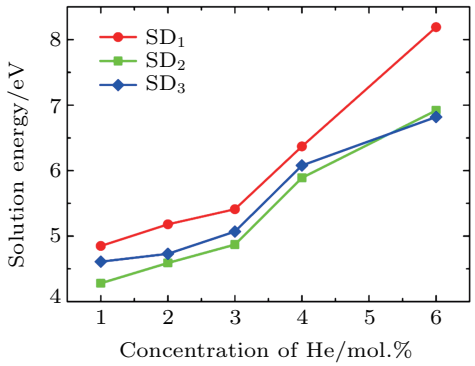


Fig. 6. (color online) Solution energies of He clusters in SDs, with the increasing concentration of He atoms in ThO_2. Three configurations of SD are considered.

Table 4. Solution energies $E^{\rm Sol}$ (in eV) and binding energies $E^{\rm B}$ (in eV) of He clusters trapped in SDs with the increasing number of He atoms.

Number of He	SD_1		SD_2		SD_3	
	$E^{\rm Sol}$	$E^{\rm B}$	$E^{\rm Sol}$	$E^{\rm B}$	$E^{\rm Sol}$	$E^{\rm B}$
1	4.85	–	4.28	–	4.61	–
2	5.18	–1.16	4.58	–1.17	4.73	–1.18
3	5.41	–1.68	4.87	–1.63	5.07	–1.59
4	6.37	–1.47	5.89	–1.36	6.08	–1.33
6	8.19	–1.15	6.92	–1.83	6.82	–2.09

To access the possibility that isolated He atoms in OISs aggregate in one SD, we also calculated the binding energies (Table 4). All of the binding energies of He clusters in the SDs are negative, suggesting that the binding process is energetically favorable. For He clusters in SD_1, the He trimer has the lowest binding energy and is the most stable cluster. For SD_2 and SD_3, a He hexamer has the lowest binding energy, indicating that He atoms tend to form a large cluster in SD_2 and SD_3.

4. Conclusion

We have performed first-principles calculations of He clustering in ThO_2. As the concentration of He atoms in ThO_2 increases, the He atoms tend to form a cluster around an OIS. A He dimer is the most stable cluster in an OIS. However, one OIS is not large enough to accommodate a large cluster, such as a He hexamer. When He atoms are located in SDs, the strain induced by the He atoms is released and the incorporation and binding energies decrease. The negative binding energies indicate that He atoms located in isolated OISs can easily aggregate in a SD. A He trimer is the most stable cluster in SD_1. Large He clusters, such as a He hexamer, can also form in SDs. For SD_2 and SD_3, even large clusters (more than six He atoms) can exist according to the calculated binding energies. Finally, our results suggest that the growth of a larger He clusters may occur by the diffusion and aggregation of Schottky defects with He atoms. Our further studies may concern the formation and diffusion of these large defects in ThO_2 with a calculation using a larger supercell. The clustering behavior of He atoms will affect the mechanical properties of ThO_2. The degradation of mechanical properties will also be investigated in further investigations.

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