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First-principles theory for helium and xenon diffusion in uranium dioxide

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ABSTRACT

The diffusion properties of He and Xe in UO_2 have been investigated, using density-functional calculations employing the projector–augmented–wave (PAW) method and the generalized gradient approximation (GGA). The migration energies corresponding to both interstitial and vacancy-assisted mechanisms have been calculated and the results for the two noble gas atoms are compared with each other. We suggest that He likely diffuses by hopping through a single vacancy with computed low migration energies smaller than 0.79 eV and its diffusivity is much higher than that of Xe. Xe has a quite large migration energy compared to He; the strain energy plays a key role in Xe diffusion in UO_2.

1. Introduction

During and after the irradiation of fuel in nuclear reactors, fission products and helium atoms are produced by nuclear fission and α-decay, respectively. Due to their low solubility, they tend to precipitate or diffuse into the gap between the fuel grains, resulting in fuel swelling [1–7]. As a result, their presence affects the mechanical properties of UO_2. The atomic transport processes of fission products and He in UO_2 are therefore of great interest for understanding the performance of UO_2 as a nuclear fuel. The diffusion characteristics of fission products have been the subject of extensive research [8–11]. From a detailed lattice structural analysis of the fission gas diffusion in UO_2 at low gas concentrations, Matzke et al. [2,9,12] have reported that some of the fission gases diffuse by proceeding via a vacancy cluster but not a single vacancy. Lawrence [13] has reported that the diffusion coefficient of fission gases is significantly affected by the defect structure of UO_2. Several experimental studies have been carried out to determine the diffusion coefficient of He in UO_2 [4,6]. Sattonnay et al. [7] have investigated the formation of He bubbles as a function of temperature and implantation condition in UO_2, and the evolution of He bubbles in spent fuel has been investigated by Ferry et al. [14]. Theoretical studies have contributed to understanding the behavior of fission gases and He in various defects of UO_2. Petit et al. [15] and Crocombette [16] have performed *ab initio* total energy calculations and investigated the stable site of some of the fission gases and He in UO_2. Freyss et al. [17] have calculated the volume variation induced by He and Xe in nuclear fuel. Recently, Yun et al. [18] have outlined the vacancy-assisted diffusion mechanism of Xe in UO_2 and supported Matzke's suggestion that a trivacancy is a major diffusion pathway of Xe. In order to better understand the difference of behavior between fission gases and He in UO_2, in this study, we investigate the diffusion properties of He and of Xe which is one of the highest fractional released fission gases in UO_2. He and Xe are chemically inert elements in group VIII of the Periodic Table, so they are expected to scarcely react with host ions of UO_2. However, there is a big difference for the atomic radius of the two atoms. The atomic radius of He is quite small, which is 0.3 Å, compared to uranium and oxygen ionic radius of 1.01 and 1.40 Å, respectively, while Xe has a much bigger atomic radius of 2.15 Å. This remarkable difference for the atomic radius of He and Xe will affect their diffusivity in UO_2, even though their chemical characteristics are similar. In this study, we therefore concentrate on a comparison of the diffusion mechanisms of He and Xe in UO_2, calculating their energy barriers and migration pathways between two trap sites. From our calculated results, we present diffusion mechanisms of He and Xe in UO_2 matrix.

2. Calculation methodology

Total energy calculations have been performed, for which we have used the PAW [19] and the GGA [20] method implemented in the VASP code [21–23]. Regardless of the fact that first-principle calculations without Hubbard *U* correction to the GGA predict a wrong electronic band structure for UO_2 [24,25], the energy information for UO_2 is almost correctly obtained by the conventional GGA method [16,17]. This also has been proved in our previous study [18]. We have calculated the formation and migration energies of defects in UO_2 using spin-polarized GGA method and

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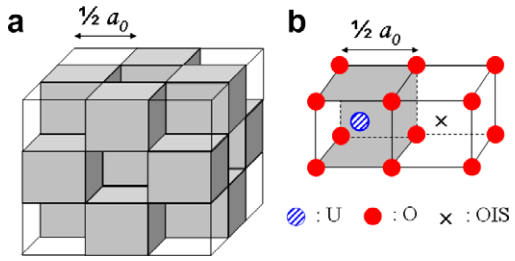

Fig. 1. (a) A $2 \times 2 \times 2$ supercell of UO_2 containing 96 atoms. (b) Oxygen atoms are located at the corners of the cubes, and uranium atoms are located at the center of an alternative cubes with grey colors. ×-Indicates the octahedral interstitial site (OIS) in fcc structure.

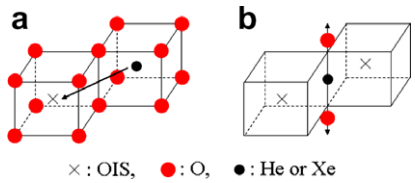

Fig. 2. (a) Movement of He and Xe between two adjacent OISs. (b) The saddle points of He and Xe and the displacement of the nearest two oxygen atoms.

obtained energy values agreed well with the experimental data. The cutoff energy of the plane-wave expansion used was up to 500 eV, and the electron charge density was computed using a $2 \times 2 \times 2$ *k*-point grid within the Brillouin zone. In this study, a $2 \times 2 \times 2$ supercell of UO_2, which has an antiferromagnetic ordering in the [100] directions [24,25], has been employed to model a defect structure of UO_2 containing He and Xe. The migration energy was calculated as the energy difference between a initial configuration and a saddle point in their diffusion pathway, as shown in Fig. 1. For all the defect structures, ionic relaxation was performed, and the force acting on each ion was relaxed until less than 0.01 eV $Å^{-1}$.

3. Results and discussion

We first investigated the interstitial diffusion mechanism of He and Xe, calculating the migration energies between two octahedral interstitial site (OIS)s, which is the body centered position of the fcc structure [18]. Fig. 1(a) shows a $2 \times 2 \times 2$ supercell of UO_2 containing 96 atoms, and Fig. 1(b) indicates the positions of host atoms and OIS which are possible sites of He and Xe atoms. In our study, an OIS was found to be the only stable site for both of the two noble atoms in a defect-free UO_2 matrix. If initially located at other interstitial sites, they move spontaneously to an OIS during atomic relaxations by the strain energy. There has been a controversy concerning the location of He. From He implantation experiment, Garrido et al. reported that He prefers to occupy OISs in UO_2 based on the assumption that 4% of uranium atoms are located in interstitial sites and 2% are uniformly distributed. If a uranium vacancy (v_U) is not located at the nearest lattice site of He_{OIS}, it is necessary to migrate over some energy barrier when He moves from an OIS to a v_U. Therefore, He would have been found more at OISs than at v_U in the low concentration limit of v_U. Our calculated results suggest that a v_U is an energetically more stable site for He than an OIS although a v_U may not necessarily constitute the majority site available to He.

Fig. 2(a) shows the migration pathways of He and Xe between two adjacent OISs, and Fig. 2(b) shows the corresponding saddle point and the displacement of the first nearest oxygen atoms along the (001) direction. We calculated the energy barrier at the saddle point by considering spin-polarization (SP), spin-orbit coupling (SOC), and the lattice expansion at high temperature. The calculated results are summarized in Table 1 and compared with experimental data.

The energy barriers between two OISs were calculated to be 2.97 eV for He and 5.29 eV for Xe in the non-magnetic, non-relativistic GGA calculations. Both energy values are relatively high compared to the experimental data of 2.00 eV [4] and 3.90 eV [2], respectively. Accounting for the relativistic SOC effect, the energy barriers obtained was 2.79 eV for He and 4.69 eV for Xe, which are decreased by 0.18 and 0.60 eV, respectively, compared to their non-magnetic results. Meanwhile, SP calculations lead to a different result for the two noble gas atoms. Xe's energy barrier is reduced to 4.48 eV from the SP–GGA calculations, but no notable energy difference was found for He. These results could be related to their atomic radii, as they are equally non-magnetic elements. The electron density of the atoms will, however, be different which could also bave an influence. The SP of UO_2 seems not to affect the movement of He with quite small atomic radius. In order to compare the strain effect of He and Xe due to the different atomic radius, we calculated the distortion of the nearest oxygen atoms of He and Xe at the saddle point, as shown in Fig. 2(b). The nearest two oxygen atoms are pushed away from their lattice sites by about 0.88 Å in the perpendicular direction to the migration pathway of Xe by the strain energy, but the displacement of the oxygens was only about 0.43 Å for He diffusion. This result shows that the strain energy of Xe is much larger than that of He and that Xe diffusion is expected to be considerably affected by the SP of UO_2, because of the large distortion of the neighbor lattice atoms. Therefore, the atomic radius of noble gas atoms is considered to be an important parameter which determines their diffusivity in UO_2. We also considered the effect of the lattice expansion at high temperature. Much improved energy values of 2.09 eV for He and 3.78 eV for Xe were obtained by using the UO_2 lattice parameter obtained at 1200 K [26], providing values very close to the experimental data as shown in Table 1.

Next, we investigated the migration pathways of He and Xe in a defective UO_2 and found that the energy barriers are remarkably decreased compared to those in a defect-free UO_2. Fig. 3(a) shows the diffusion pathways for He between two OISs by hopping through a v_U or oxygen vacancy (v_O), and the corresponding energy barriers are 0.79 and 0.41 eV, respectively. The most stable site for He was calculated to be a v_U among OIS and single vacancies, and a v_O was the most unstable. On the other hand, the OIS was found to be most unstable for Xe. The energy difference between two configurations of Xe_{OIS} and Xe_U, and Xe_{OIS} and Xe_O were calculated as 2.90 and 6.83 eV, respectively, as shown in Fig. 3(b).

This relatively large energy difference implies that, if Xe is trapped at v_O or v_U, it can hardly move to a new location. As a result, the diffusivity of Xe is expected to be much lower than that of He. Experimental studies also reported that the diffusion coefficient of He is much higher than that of Xe [4]. Meanwhile, as mentioned previously, the strain energy of Xe is much larger than that of He, so we examined the strain effect of Xe in its diffusion. We found that Xe is more likely to be located at a vacancy cluster than a single vacancy, so the large strain energy of Xe contributes to

Table 1
Calculated energy barriers (eV) of He and Xe between two adjacent OISs.

	PAW–GGA calculations				Experiment
	NM	SP	SOC	a_0 = 5.53 Å	
He*	2.97	2.97	2.79	2.09	~2.00 [4]
Xe [18]	5.29	4.48	4.69	3.78	3.90 [2]

* This work.

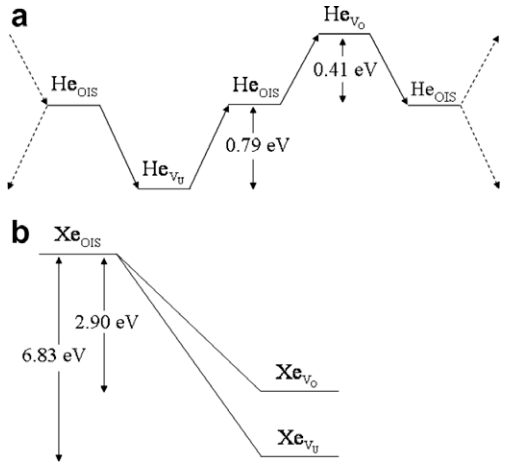

Fig. 3. (a) Migration pathways of of He between two OISs by hopping through a single vacancy. (b) The energy differences between two configurations of Xe_{OIS} and Xe_U, and Xe_{OIS} and Xe_O.

form a vacancy cluster. Fig. 4 shows that, if a v_O is created at the second nearest lattice site when Xe is trapped at a v_U, the Xe_U pushes the first nearest oxygen atom into the v_O and finally forms an extended defect Xe_{UO}.

This result implies that vacancies can be clustered not only by the hopping around of single vacancies but also by the strain energy of Xe in UO_2. Through the vacancy-clustering process induced by the strain energy of Xe, Xe-vacancy complexes of Xe_{UO} and Xe_{UO_2} can be formed in UO_2. We also calculated the binding energy needed for a Xe-vacancy complex to be dissociated and found that Xe_{UO_2} is most easy to be separated because of its lower binding energy of 1.39 eV among Xe-vacancy complexes [18].

These results agree well with the experimental studies [2,9,27]. Matzke observed that large variations in the concentration of either oxygen or uranium vacancies did not affect single gas atom diffusion and suggest that trivacancy (v_{UO_2}) is the lattice location and diffusion mechanism of heavy rare gases in UO_2. In order to better understand the vacancy-assisted diffusion mechanism of Xe in UO_2, we suggest a major diffusion pathway of Xe shown in Fig. 5 [18]. It is assumed that Xe is located at a trivacancy as shown in Fig. 5(a) from the following requirements: Xe prefers to be located at a vacancy cluster with a single vacancy [18], trivacancy is the simplest and most dominant vacancy cluster among the irradiation-induced defects [2], and the electrical charge neutrality of trivacancy is stable for Xe which is one of the inert gases. Fig. 5(b) indicates the process that Xe-trivacancy complex is separated with Xe-divacancy and a single oxygen vacancy with their lowest binding energy of 1.39 eV. A uranium vacancy comes into the configuration and the barrier-less movement of Xe occurrs by the strain energy in Fig. 5(c) and (d), respectively. Apparently, the defect configuration in Fig. 5(d) is not exactly a Xe-trivacancy complex, and there are two uranium vacancies despite the Xe's

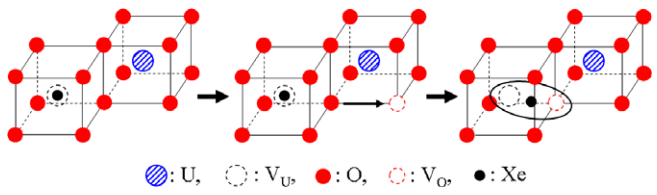

Fig. 4. A vacancy-clustering process induced by the strain energy of Xe. If a v_O is created at the second nearest lattice site of Xe_U, the first nearest oxygen atom is pushed into the v_O by the strain energy of Xe. Finally, Xe_{UO} is formed.

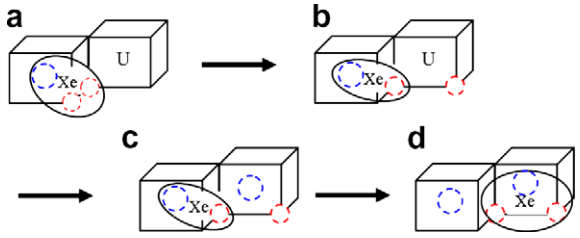

Fig. 5. The vacancy-assisted mechanism of Xe in UO_2: (a) Xe is located at a v_{UO_2}, (b) a v_O is separated from an Xe_{UO_2}, (c) a v_U come into the configuration, (d) Xe moves to the center of the v_{UO_2} by the strain energy.

location at the center of the trivacancy. In the vacancy mechanism of Xe in UO_2, the rate determining process is the movement of uranium vacancy which is known to require much higher migration energy than oxygen vacancy [2,18,27]. However, we found in our previous study that the migration energy of a uranium vacancy is lowered by about 1 eV and needed to be 2.19 eV, via the effective movement of a vacancy cluster with oxygen vacancies together [18].

In this work we have not taken into account the Van der Waals interactions. A well-known shortcoming of the standard exchange–correlation functional (LDA and GGA) used in density-functional theory is that they do not include long-range correlation and therefore fail to describe Van der Waals bonded systems accurately [28]. For instance, the binding in rare gas dimers is strongly overestimated by the LDA. Therefore Van der Waals effects become very important to describe larger molecular systems with rare gas atoms. However, it can be considered small enough to be ignored in this work, because we have focused on the DFT calculations for a single noble gas atom.

4. Conclusion

We found that the computed migration energy depends on SOC, SP, and the lattice expansion at high temperature for both noble gas atoms. However, we found that the SP of UO_2 does not affect the He diffusion. Furthermore, the distortion of the nearest oxygen atoms at the saddle point between two OISs was calculated to be much larger for Xe than for He. The diffusion pathways of noble gas atoms are consequently strongly affected by the strain energy derived from the relative size of their atomic radius. Apart from the atomic radii, He and Xe differ in their electron densities. These differences are accounted for in the *ab initio* calculations but we have not attempted to specify their influence on the diffusion process. From all the calculated results, we find that the dominant diffusion pathway of He is to hop through a single vacancy and Xe is likely to diffuse through the processes of vacancy-clustering and–declustering.

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