



First-principles energetics of rare gases incorporation into uranium dioxide



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ABSTRACT

First-principles density functional theory–generalized gradient approximation methods have been used to calculate the energetics (incorporation energy, formation energy and binding energy) of rare gases (He, Ne, Ar, Kr and Xe) at the three incorporation sites (octahedral interstitial, uranium and oxygen vacancies) of uranium dioxide. The Hubbard parameter U and van der Waals corrections have been used to describe the strongly correlated electronic behavior of uranium 5f electrons and the weak interactions of rare gases, respectively. The results indicate that the energetics of rare gases depend significantly on the incorporation sites and on the atomic properties such as atomic radius. All rare gases considered here are energetically unfavorable at the three incorporation sites. However, rare gases exhibit significant binding ability to both U and O vacancies. The main trends of relative stability of rare gases generally reflect a size effect: the rare gases become more unstable with increasing atomic number. Electronic structures of these systems containing rare gases also exhibit general trends in their relative stability and charge-transfer character.

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1. Introduction

Uranium dioxide (UO_2) is the standard nuclear fuel, whose properties play a crucial role in the reliability and safety of nuclear reactors. Therefore, many experimental and theoretical studies have been conducted on the structures and properties of this oxide under irradiation. Among them, the behaviors of fission products have been extensively investigated because fission products often play a decisive role in the material properties of nuclear fuels. An outstanding example is the formation of gas bubbles, which can cause swelling, microstructure alteration and properties degradation of materials [1–3]. In fact, among the fission products, rare gases have attracted the most attention because of their significant impact on fuel performance. However, to our knowledge, systematic experimental characterization and analysis of the behavior of rare gases in UO_2 have been rarely reported. This scarcity can be attributed to the difficulties in preparing and handling high-quality radioactive UO_2 samples, and in identifying the states of rare gases by means of conventional analysis techniques. Available experimental data on rare gases in UO_2 mainly relate to the release and distribution of gas bubbles [4,5]. Some experimental techniques such as X-ray diffraction (XRD), transmission electron

microscopy (TEM), thermal desorption spectroscopy (TDS) and secondary ions mass spectroscopy (SIMS) have been used to indirectly probe the influence of rare gases on structural changes in nuclear fuels [1,6–9]. Generally speaking, the results were more statements of macroscopical phenomena than explanations of microscopic mechanisms. The inherent behaviors of rare gases and their effects on material properties are still not completely understood. Consequently, further studies are required to elucidate the microscopic behavior of rare gases in UO_2 .

An effective solution to complement experiments and serve as a predictive tool in understanding the microscopic behavior of rare gases in UO_2 is the use of computational techniques [10]. Among them, first-principles calculations based on density functional theory (DFT) have been widely used for the behavior of rare gases in UO_2 , in particular, the behavior of Xe for understanding the large swelling and property alteration of UO_2 . Earlier DFT calculations of Xe atom in UO_2 were performed without any correction for the strong on-site Coulomb repulsion among the localized U 5f electrons [11–13]. Although those DFT methods reasonably reproduced the lattice parameter, bulk modulus and cohesive energy of UO_2 , their results indicated a notable variation in incorporation energy varying from 1.43 eV to 19.0 eV, and cannot be well explained. Afterwards, Yu et al. calculated the formation energies of Xe in a variety of sites in UO_2 using GGA + U [14]. Here, U is Hubbard parameter for describing strongly correlated behavior of U 5f

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electrons. The authors found that Xe prefers to be trapped by a Schottky site regardless of relaxation schemes. Nerikar et al. predicted the stability of Xe in $\text{UO}_{2\pm x}$ by means of DFT and DFT + U , and found that the relatively stable site depended on stoichiometry of $\text{UO}_{2\pm x}$ [15]. For Xe, the most stable solution site was the bound Schottky for UO_{2-x} and UO_2 , and the uranium vacancy for UO_{2+x} . For Cs, the preferred solution site was the bound Schottky for UO_{2-x} , the divacancy trap site for UO_2 and the uranium vacancy for UO_{2+x} . The authors also attributed the differences of incorporation energy in DFT and DFT + U to the limitation of DFT to capture the localized behavior of U 5f electrons. Thompson et al. performed a series of DFT + U calculations to explore the incorporation energy of Xe at the different sites of UO_2 [16], and compared their results with literature values obtained by classical potential, pure DFT and DFT + U methods. The authors stated that the correct ground state of UO_2 was essential for the calculations of defect energetics. Subsequently, Liu et al. reviewed atomic scale simulations aimed at elucidating Xe transport in UO_2 [17], with focus on DFT and DFT + U works compared to experimental findings. Several Xe migration mechanisms were proposed but not conclusively determined. The discrepancies among different authors' calculations resulted not only from DFT methods, but also from the computational details such as supercell size, relaxation scheme, defect configuration, stoichiometry, etc. Additionally, other factors related to real conditions such as temperature and sample state were needed to be considered to connect experimental results. More recently, Liu et al. conducted molecular dynamics simulation on the behavior of Xe bubbles in UO_2 [18], and found that the small Xe bubbles (1–5 Xe atoms) nucleus at grain boundaries had much lower formation energy compared to that of similar sized bubbles in the bulk. However, when the Xe bubbles grew into larger sizes of about 20 Xe atoms, the Xe bubble formation energy at grain boundaries approached that of similar sized bubbles in the bulk. In any case, a combination of atomic and mesoscopic scale calculation is required to understand the behavior of isolated Xe atom, the clustering and formation of Xe bubbles, and the influence of Xe on the material properties of UO_2 [10].

Apart from Xe, other two important transmutation products He and Kr have also been widely investigated using different scale computational techniques [19–21]. The prominent feature of DFT + U calculation results is that the relative stability decreases with the increasing atomic number of rare gases. This can be understood based on the reasonable assumption that strain effect mainly resultant from size effect plays a crucial role in the relative stability of those closed shell atoms, whereas electronic interaction is supposed to play the secondary one. In fact, the general trends in incorporation energy of rare gases (He, Ne, Ar, Kr and Xe) were initially obtained using DFT + U method by Thompson et al. [16] and hybrid DFT method by Ma et al. [22], respectively. However, the large variation of energy values in the above two works and other works outlined earlier intrigue us to conduct a systematic calculation on the energetics of rare gases in UO_2 . After a detailed analysis of the published results, we consider that four factors are needed to account for the reasonable description of rare gases behavior in UO_2 . First, the reasonable treatment of localized U 5f electrons is necessary. Almost all pure DFT calculations give a wrong metallic ground state instead of a semiconducting ground state of UO_2 . Among all improved DFT methods, DFT + U method provides very good result of band gap of bulk UO_2 [23,24]; other methods such as hybrid DFT and dynamics mean-field theory (DMFT) are not so efficient in the defect systems despite they may provide more reasonable ground state of perfect UO_2 crystal. For the theoretical studies of defect behavior in UO_2 and other actinide oxides, DFT + U method is the major choice in the literature as the result of compromise between computational efficiency and accuracy. Second, relaxation scheme is very sensitive to the energy values of

defects in UO_2 . An outstanding example is the most widely calculated incorporation energy of octahedral interstitial O in UO_2 , which spans from largely negative -2.44 eV to slightly positive 0.1 eV in the literature [25]. An important reason for the discrepancy is the choice of relaxation scheme, e.g., “volume only” with symmetry constraint or “complete” relaxation without symmetry constraint. Generally, complete relaxation is required for the systems containing defects because anisotropic distortion may occur in the systems, especially for the cases that incorporated impurity atoms break the symmetry of the host. Third, as well known, standard DFT method fails to correctly describe the long-range weak interactions. Almost all DFT-based treatments of rare gases in UO_2 have neglected van der Waals (vdW) interaction, which may be an important factor in the incorporation energy and the electronic interaction between rare gases and UO_2 . Finally, the delicate differences in the electronic interaction between different rare gases and UO_2 had been scarcely reported because rare gases had long been considered as inactive elements. However, increasing experimental and theoretical studies have provided evidence for chemical bonding of rare gases with materials, also including actinide-based materials [26]. Therefore, a careful calculation regarding the electronic interaction can facilitate the understanding of fundamental behavior of rare gases in UO_2 .

In our previous studies [27,28], we calculated the energetics of a series of nonmetallic impurity atoms (e.g., H, He, B, C, N, O, F, Ne, Cl, Ar, Kr and Xe) in PuO_2 by means of DFT + U methods. The results indicate that the energetics of impurity atoms depend significantly on the incorporation sites and on atomic properties such as atomic radius and electron affinity. The trends of incorporation energies of rare gas atoms generally reflect a size effect. Although UO_2 and PuO_2 have the same crystal structure under normal conditions, the behaviors of their 5f electrons are different [29,30]. The 5f electrons in Pu are determined to be more localized than those in U. A typical feature resultant from the difference is that UO_2 can be relatively easily oxidized to higher oxides (e.g., U_4O_9 , U_3O_8 and UO_3) [31]; however, whether PuO_2 could be oxidized to $\text{PuO}_{2.25}$ remains in debates [27,32]. Additionally, the difference in the behavior of 5f electrons may lead to the difference of defect behavior in the two dioxides. In the current work, we calculate the energetics of rare gases in UO_2 using DFT + U method in order to obtain the general trends of their relative stability. The four calculation factors mentioned above are taken into account for the reasonable description of rare gases behavior in UO_2 . We expect that these general trends in this work constitute the foundation of further investigations on the multi-scale simulations of rare gases behavior in UO_2 .

2. Computational details

UO_2 crystallizes in the face-centered cubic (fcc) fluorite (space group: $225/Fm\bar{3}m$) structure. Here, we use its conventional cell (i.e., U_4O_8 with a lattice parameter of 5.470 Å) to build calculation models containing rare gases, as shown in Fig. 1. Three incorporation sites of rare gases, i.e., octahedral interstitial, U and O vacancy, are considered, corresponding to $\text{U}_4\text{O}_8\text{X}$ (X: He, Ne, Ar, Kr and Xe), $\text{U}_3\text{O}_7\text{X}$ and $\text{U}_4\text{O}_7\text{X}$, respectively. These three sites are the ones most widely studied in electronic structure calculations concerning the basic behavior of impurity atoms in oxide-type nuclear fuels. More complicated defects, such as di-vacancies, multi-vacancies, or other defect clusters which might accommodate rare gases and which require a larger supercell to build the defect models, are not considered in the current works. As a matter of fact, our calculation tests on the size of models show that the incorporation energies of octahedral interstitial O in U_4O_8 and $\text{U}_{32}\text{O}_{64}$ ($2 \times 2 \times 2$ U_4O_8 supercell) agree within 8%, which justifies the present calculation models.

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