Charge states of point defects in plutonium oxide: A first-principles study

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ABSTRACT

The stability of charged defects in PuO_2 are systematically investigated by quasi-annealing simulations based on local spin density approximation (LSDA) + U calculations. The formation energies of intrinsic (Frenkel and Schottky pairs) and extrinsic (single vacancy or interstitial) defects at different charged states are calculated and presented. According to our results, the noninteracting oxygen Frenkel pairs made of the association of doubly charged defects are the most favorable form of intrinsic defects, the formation energy of which is in good agreement with experimental values. The negative charged oxygen interstitial (I_O^{2-}) and positive charged oxygen vacancy (V_O^{2+}) defects have the lowest formation energies at oxygen-rich and oxygen-poor environments, respectively, and thus are the most commonly seen extrinsic defects. Both the existences of oxygen vacancy and oxygen interstitial induce new electronic states in the band gap of stoichiometric PuO_2, showing doping effects.

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1. Introduction

Plutonium-based materials have been attracting vast attentions from various scientists for several decades, due to their technological and environmental implications [1–8]. Plutonium dioxide (PuO_2) is an important ingredient of a mixed oxide (MOX) fuel for fast breeder reactors, the physical, chemical, and mechanical properties of which are important for nuclear engineering [9–11]. Also, PuO_2 has long been the compound of choice for plutonium reuse, separation, and deposition in long-term repositories, due to its reliable stability with respect to oxidation [12]. Based on these backgrounds, many studies have been performed to investigate various properties of PuO_2 [3–8,13–19]. However, most of these studies place their focuses on stoichiometric PuO_2, and knowledge about non-stoichiometric PuO_2 is comparatively insufficient. On the other hand, non-stoichiometric PuO_2 widely exists in reality under various external environments such as radiation, high temperature, high gaseous pressure, and humidity. Recently, it is also revealed that under a humid environment, PuO_2 can react with water forming higher oxides PuO_{2+x} [20,21]. To understand the physical properties of non-stoichiometric PuO_2, the formation of intrinsic defects as well as their charge states need to be investigated first.

Different from stoichiometric PuO_2, whose structural and electronic properties can be easily measured on fabricated samples, measuring the defect concentrations and formation energies of non-stoichiometry state is quite tricky and difficult [22,23]. The experimental measurements need to be carefully performed on non-stoichiometric samples. For example in the case of UO_2, the inherent difficulties in the measurement conditions have caused dispersed results [24,25]. Theoretically, the most important feature of plutonium-based materials is the strong on-site Coulomb repulsion of the 5f electrons. Conventional density functional theory (DFT) of electrons based on the local spin density approximation (LSDA) or generalized gradient approximation (GGA) do not take into account such strong on-site correlations beyond the homogeneous electron gas, and therefore cannot reasonably describe the ground-state electronic structures, where AnO_2 ($An =$ U, Np, Pu, and Am) are all described to be ferromagnetic conductor instead of Mott insulators [4,8,26–29]. Methods that go beyond standard DFT exchange correlations, such as DFT + U [30,31], hybrid DFT [15], self-interaction corrected local density approximation (SIC-LDA) [32], and dynamical mean-field theory (DMFT) [33], can yield a band gap in these 5f materials. For small simulation systems, such as the 3-atom primitive cell or 12-atom unit cell, most of these methods could reproduce satisfactory quantities with respect to

experiments, balancing the efficiency and accuracy. While in study of non-stoichiometric systems (including defects), one has to build the large supercells to get rid of the effects brought about by periodic boundary condition. In this case, the LSDA + U method is irreplaceable, because it can give reliable data while maintaining high efficiency. Briefly, the LSDA + U approach can be understood as adding a penalty functional to the LSDA total energy expression that forces the on-site occupancy matrix in the direction of idempotency [30,31].

The incomplete understanding of physical properties for non-stoichiometric plutonium oxides motivates us to carry out the present study. Especially, in comparison with the vast investigations on behaviors of intrinsic defects in another important actinide dioxide UO_2 [34−44], few studies have been carried out for PuO_2. Thus in present work, we systematically study the energetics of intrinsic point defects with different charge states in PuO_2. The atomic configurations around the point defects, as well as the projected electronic density of states (PDOS) and charge density distribution of the defective systems, are compared and discussed. From the calculated total energies of supercells containing specified defects, we deduce the formation energies of intrinsic point defects, i.e., Frenkel and Schottky pairs. The influences of various external environmental factors will be reflected in the micro Fermi level, which may change between the valence band maximum (VBM) and conduction band minimum (CBM). We have also tracked this microscope process, where the formation energies of extrinsic point defects, including single oxygen-related and plutonium-related vacancies or interstitials, are expressed as functions of the Fermi level in oxygen-rich and -poor conditions, respectively. The point defect model (PDM) in closed and opened regimes allows us to assess the concentrations of defects in plutonium dioxide and their variations with stoichiometry. We believe that these theoretical results are essentially prerequisite for explaining and predicting the behavior of plutonium dioxide in engineering applications, and should constitute an interesting benchmark against future experimental or theoretical studies. In the next section, we will discuss the calculation method briefly. The calculation results and discussions are presented in Section 3. Finally in Section 4, we give a summary of our work.

2. Calculation method

The DFT total-energy calculations are carried out by the projected-augmented-wave (PAW) method [45] using the LSDA exchange correlation functional as implemented in the Vienna *ab initio* simulations package (VASP) [46,47]. The plutonium $6s^2 7s^2 6p^6 6d^2 5f^4$ and oxygen $2s^2 2p^4$ electrons are treated as valence electrons. A $2 \times 2 \times 2$ supercell (containing 96 atoms) has been employed to model the defect formation in PuO_2. For the 96-atom supercell calculations, a $4 \times 4 \times 4$ k-point mesh is used in Brillouin zone (BZ) integrations [48]. Our test calculations show that such a k-points mesh could guarantee an energy convergence of 0.1 meV/ atom. The electron wave functions are expanded in plane waves up to a cutoff energy of 520 eV, which is enough to make sure that errors in the formation energies of different defects are less than 1 meV. The $1k$ antiferromagnetic (AFM) spin configuration, where the magnetic moments of Pu atoms are oriented along $\langle 001 \rangle$, is applied to PuO_2. The spin-polarized LSDA + U method formulated by Dudarev et al. [30,31] is employed to remedy the failures raised by LSDA in describing the strong intra-atomic Coulomb interaction among the Pu $5f$ electrons. In the present study, we set the values of U and J parameters to be 4.7 eV and 0.7 eV respectively, in consistent with previous theoretical studies on PuO_2 [4, 8,49,50]. The quasi-annealing (QA) simulation method proposed by Geng et al. [51] is used to conquer the possible occurrence of multiple minima

in the process of calculations. The detailed steps are: (1) Set a self-consistent field (SCF) tolerance $\delta E = 0.05$ eV with an energy convergence of 1 meV/atom. The ions are updated and moved according to the conjugate-gradient algorithm with the length of the trial step $\delta r = 1.0$. (2) Relax the structure. (3) Reduce δE and δr slightly, restore the structure and go to step 2 and repeat the procedure at least five times until δE and δr reach the target precision of 0.001 eV and 0.2, respectively. (4) Slightly distort the structure, go to step 1 and repeat the whole process until no lower state can be found. In our present study, the final energy convergence is 0.1 meV/atom. A total number of four independent QA runs are performed for the supercell calculations. The obtained equilibrium unit cell volume of PuO_2 is 153.53 Å^3. The electronic band gap is found to be ~1.70 eV, in consistent with previous experimental and theoretical results [5,32,52]. During calculations of defective structures, the shape and size of the supercell are fixed while the fractional atomic coordinates are relaxed until the Hellmann−Feynman forces on each atom are less than 0.02 eV/Å.

Although the spin−orbit coupling (SOC) is important for certain properties of heavy-metal compounds [53,54], it has been numerically found [27,28] and physically analyzed [13,14] that inclusion of the SOC has little effect on the bulk and one-electron properties of PuO_2. Our test calculations also show that inclusion of SOC only increase the optimized lattice constant by 0.7% and the bulk modulus by about 0.5 GPa for PuO_2. Therefore in our following calculations for defective PuO_2, the SOC is not included.

Four kinds of point defects are considered for PuO_2: oxygen vacancy (V_O), oxygen interstitial (I_O), plutonium vacancy (V_{Pu}), and plutonium interstitial (I_{Pu}). The structural models are depicted in Fig. 1. The charge states from −2 to +2 and from −4 to +4 are considered for oxygen and plutonium defects respectively. The additional charge is modeled by adding or removing electrons from the supercell. From the energies calculated for the defect-free and defect-containing boxes, one can obtain the formation energies of the isolated point defects with charge q as follows:

$$E^f(X^q) = E_X^{N\pm 1} \pm \mu_x - E_\varnothing^N + q(E_{VBM} + \varepsilon_F + \Delta v), \qquad (1)$$

where $E_X^{N\pm 1}$ is the total energy of the supercell with defect X, μ_x is the chemical potential of atom x with a positive (negative) sign for vacancy (interstitial) defect and here we select the δ-Pu and oxygen molecular O_2 as the reference states, $E_\varnothing^N$ is the free energy of the defect-free PuO_2 supercell, E_{VBM} refers to the VBM, and ε_F is the chemical potential of electrons (or the Fermi level) with respect to the VBM, which thus can take values from zero to the width of the band gap in the perfect crystal. The shift of the VBM in a defect supercell Δv takes the change of the VBM caused by taking the defect into account, whose value can be obtained by a macroscopic average technique [55,56] through calculating the difference between the average electrostatic potential in a bulk-like environment of the defective supercell and the average electrostatic potential in the defect-free supercell.

According to the thermodynamic equilibrium condition, the sum of the chemical potentials of atoms in PuO_2 must be equal to the heat of formation to ensure the stability of the compound PuO_2. This condition can be expressed as

$$\Delta H(PuO_2) = \Delta \mu_{Pu} + 2\Delta \mu_O. \qquad (2)$$

where $\Delta H(PuO_2)$ is the formation enthalpy of PuO_2. The modification of chemical potential for oxygen (plutonium) under O-rich (Pu-poor) condition and O-poor (Pu-rich) condition are $\Delta \mu_O = 0$ [$\Delta \mu_{Pu} = \Delta H(PuO_2)$] and $2\Delta \mu_O = \Delta H(PuO_2)$ [$\Delta \mu_{Pu} = 0$], respectively.

The formation energy of an oxygen or plutonium Frenkel-pair can be deduced by summing up the formation energies of a