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Hydroxylation-induced surface stability of AnO_2 (An = U, Np, Pu) from first-principles

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ABSTRACT

The relative stabilities of clean and hydroxylated surfaces of three actinide dioxides (AnO_2, An = U, Np, Pu) have been investigated using first-principles methods within the DFT + *U* framework. In the case of the clean surfaces, the calculated surface energies are consistently the lowest for the (111) surface for all three AnO_2 compositions, followed by the (110) and (100) surface energies. In the case of UO_2, for instance, the calculated surface energies are 0.78, 1.05, and 1.47 J/m^2 for the (111), (110), and (100) surfaces, respectively, reinforcing the well-established surface energy trend for metal-dioxides: (111) < (110) < (100). Dissociated water, at one monolayer coverage, is adsorbed preferentially onto the (100) surface for all three AnO_2 systems. In the case of UO_2 the water adsorption energy on the (100) surface (-1.34 J/m^2) is almost four times higher than the adsorption energy on the (111) surface (-0.35 J/m^2), and almost twice as large as the adsorption energy on the (110) surface (-0.77 J/m^2). Similar trend in the adsorption energies is observed for both NpO_2 and PuO_2. As a result, the relative stability of the hydroxylated AnO_2 (An = U, Np, Pu) surfaces changes to (100) < (110) < (111). The effects of the geometric relaxations on the clean and hydroxylated surfaces are discussed.

1. Introduction

Among the actinide-based systems, actinide-dioxides (AnO_2, An = U, Np, Pu) have been, by far, the most intensely studied both experimentally and theoretically [1–16], not only because of their technological relevance in the nuclear power industry, but also because of their significance from fundamental scientific point of view. From a technological perspective, the AnO_2 surface structure and reactivity are extremely important subjects, because they affect a variety of processes ranging from fabrication of the nuclear fuel pellets to spent-fuel storage in water, or long-term disposal of the spent fuel in a geologic repository [17]. Consequently, a substantial body of experimental investigations has been completed in order to characterize the surface structure and reactivity (surface–water interaction) of AnO_2 (An = U, Pu, and surrogates) systems [18–30].

The fundamental scientific interest in AnO_2 materials is related to the presence of partially occupied 5*f* orbitals. Depending on the electronic and structural environment, as well as on external parameters, such as temperature or pressure, the 5*f* electrons are often situated at the boundary between localized and itinerant behavior [31,32]. This gives rise to a variety of unusual physical properties [6,33–36], pushing the limits of current theoretical capabilities, regarding the description of these materials using first-principles methods. Atomic-scale modeling of AnO_2 surfaces, based on empirical potentials has revealed several important aspects related to surface defect configurations and modification of crystal morphologies through hydroxylation [37–39]. First-principles studies of AnO_2 surfaces are rather scarce in the literature. Only few authors have completed density-functional calculations in the standard, local-density (LDA), or generalized gradient approximation (GGA) in order to explore the UO_2 and PuO_2 surfaces and their interaction with water or oxygen [1,40–43]. We are not aware of surface calculations performed on the NpO_2 system. Furthermore, it seems that only Jomard and Bottin [44] went beyond standard LDA/GGA, and used the so called DFT + *U* approach in order to capture the effects of electronic correlations on the PuO_2 surfaces. They showed that a proper description of the correlated 5*f*-states is required in order to capture the correct surface stabilization of PuO_2.

In this paper, we investigate the complex problem of surface energetics and surface–water interaction in AnO_2, using first-principles methods within the density functional theory (DFT), with the inclusion of the Hubbard *U* parameter in the calculations. Based on surface energy calculations, we determine the relative stability of the dry, low-index (111), (110), and (100) surfaces of AnO_2 (An = U, Np, Pu) and the effect of dissociative water adsorption on the stability of these surfaces.

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2. Methodology

2.1. Computational methods and parameters

The results presented in this article have been obtained using the projector augmented wave (PAW) [45,46] method within density functional theory (DFT) [47,48] as implemented in the Vienna Ab-initio Simulation Package (VASP) [49–52]. The exchange-correlation potential was approximated by the generalized gradient approximation (GGA), as parameterized by Perdew, Burke, and Ernzerhof (PBE) [53]. The standard PAW potentials, supplied with the VASP code, were employed in the calculations [45,46]. After a series of convergence tests on different bulk AnO_2 compositions, to ensure a precision better than 1 meV/formula-unit (f.u.), the cut-off energy for the plane wave basis was set to 500 eV, and the Brillouin zone (BZ) was sampled by a $4\times4\times4$ Γ-centered Monkhorst–Pack (MP) k-point mesh [54]. The convergence of the self-consistent cycles was assumed when the energy difference between them was less than 10^{-4}eV.

In order to capture the correct behavior of the localized *f* electrons of U, Np, and Pu, an orbital-dependent, on-site Coulomb potential (Hubbard *U*) was added to the Hamiltonian within the so-called DFT + *U* method [55,56]. In this work, the Hubbard *U* and exchange (*J*) parameters are treated as empirical parameters and are selected from values that were used previously in the literature, such that a satisfactory agreement between experiment and theory is obtained regarding the electronic properties of actinide-containing systems. The calculations have been performed with the following values: $U=4.5$ eV, $J=0.5$ eV for uranium [12,55,57–59] and $U=4.0$ eV, $J=0.4$ for neptunium [15,16] and plutonium [2,13,44]. In order to assess the correctness of these values vis-a-vis the electronic structure of the bulk materials, we compare the calculated band gaps (E_g) and densities of states (DOS plots are given in the Supplementary Material) with results published in the literature. The calculated band gaps for the ferromagnetic (FM) states of the AnO_2 series, An = U, Np, and Pu are 2.5, 2.5, and 2.1 eV, respectively. We note that the gap values for UO_2 and PuO_2 are in good agreement with the ones calculated by Scuseria and Martin [7,60] using the screened hybrid density functional of Heyd, Scuseria, and Ernzerhof (HSE) [61,62]. For NpO_2 we obtained a band gap which is 0.6 eV narrower than the one calculated in Ref. [7]. From a comprehensive search of the literature we recognize that the theoretical band gaps for AnO_2 (An = U, Np, Pu) vary between 2 and 3 eV, and our result fits well within this range.

The AnO_2 surfaces were simulated by periodic slab geometries constructed using the unit cell parameters obtained for the optimized bulk structures ($a_U=5.547$ Å, $a_{Np}=5.499$ Å, $a_{Pu}=5.457$ Å). In each slab (with and without adsorbed water) the atomic positions were allowed to relax until the Hellmann–Feynman forces were less than 0.02 eV/Å. In this work, the (1×1) surface unit cells of the low index (111), (110), and (100) surfaces were investigated. The slab representing the (100) surface consists of alternating layers of An and O; therefore, it possesses a repeated sequence of dipole moments perpendicular to the surface [63]. In reality, such a surface cannot exist because the presence of a dipole moment perpendicular to the surface leads to the divergence of the electrostatic potential as the thickness of the slab increases. In order to eliminate this instability, half of the O atoms from the top of the slab were moved to the bottom of the slab. This type of "half-monolayer-oxygen configuration" has been observed on the (100) surface of UO_2, using scanning tunneling microscopy [22]. To simulate the adsorption of water, we used the double-sided adsorption model, as described by Skomurski et al. [41]. In order to ensure a consistent k-point density for the bulk and slab calculations, the Brillouin zones of the slabs representing the (111), (110), and (100) surfaces were sampled by Γ-centered meshes of $6\times6\times1$, $6\times4\times1$, and $4\times4\times1$ k-points, respectively. We note, that our calculated structures are not necessarily minima as we did not perform vibrational calculations.

The use of an explicitly orbital-dependent Hamiltonian (DFT + *U*) for the treatment of the correlated electrons introduces orbital degrees of freedom in the calculation, which leads to *multiple self-consistent solutions*. For instance, in the case of UO_2, the two localized electrons of the U^{4+} ion can be distributed in 21 different ways over the 7 (spin-degenerate) *f* orbitals and for each configuration, a self-consistent solution can be obtained. Since, in many cases, the energies corresponding to these *metastable* states differ by several eVs, it is crucial to identify the electronic configuration corresponding to the ground state. One method of achieving this is to carry out calculations using all possible orbital occupations as initial density matrices and then, based on the fact that the DFT + *U* (for fixed *U*) is a variational method, chose the lowest energy solution as the ground state configuration [2,12,64–66]. An alternative method proposed by Meredig et al. [67] for locating (or at least approximating) the ground state is the so called "*U*-ramping" method. In this approach, the Hubbard-*U* parameter is gradually increased until integer band occupations are obtained, and then the calculation is continued with the nominal value of *U*. In this method, at each increment of the Hubbard-*U*, the previously obtained density matrix (charge density/wave functions) is applied.

The abovementioned methods for locating the low-energy solution in a DFT + *U* calculation lead to similar results. However, because we have used a DFT code (VASP) that does not allow for the direct control of the density matrices, we have employed *U*-ramping in the calculations. Furthermore, the *U*-ramping method appears to be computationally more efficient than the method based on the exhaustive enumeration of the orbital occupancies. Following the description of Meredig et al. [67], we started all calculations with a diagonal occupation matrix corresponding to $U=0$ and gradually increased *U* by 0.1 eV until all bands were integrally occupied. After the insulating state was reached, we performed the calculations with the nominal values of the screened Coulomb potentials (Hubbard-*U*s) specified earlier. In order to reach the insulating state (fully-occupied bands), the *U*-ramping method required between 7 and 18 DFT + *U* calculations for each slab, depending on the surface orientation and the actinide element present in the system. The minimal values of the *U* parameter for which integer band occupations were obtained are listed in Table 1.

For consistency between the bulk and slab calculations and to avoid complications arising from modeling the antiferromagnetic (AFM) ordering of the magnetic moments, we have only considered the simple ferromagnetic (FM) configuration. The choice of the FM order is justified by the explicit calculations carried out by a number of authors, who showed that, for AnO_2, the difference in the total energy between the FM and AFM solutions is of the order of tens of meV [2,68,69]. Furthermore, we find good agreement between our PuO_2 surface energies calculated for the FM configuration and the AFM results of Jomard and Bottin [44]. This suggests that the spin-order has little influence on the systems and properties under study. More details about this comparison are given in Section 3. The calculations were performed without any symmetrization constraints on charge density [70].

2.2. Surface energies

The surface energy is defined as the energy required for separating the bulk material into two, semi-infinite slabs. In principle, using this

Table 1
Minimal values of the Hubbard-*U* parameter for which the electronic bands are integrally occupied, along with the slab thicknesses.

Surface	UO_2		NpO_2		PuO_2	
	U (eV)	d_{slab} (Å)	*U* (eV)	d_{slab} (Å)	*U* (eV)	d_{slab} (Å)
(111)	1.5	17.37	0.8	17.34	1.8	17.18
(110)	1.0	9.70	0.7	9.62	1.5	9.59
(100)	1.4	16.00	0.7	15.88	1.4	15.76