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Relaxation of the (1 1 1) surface of δ-Pu and effects on atomic adsorption: An *ab initio* study

Raymond Atta-Fynn, Asok K. Ray*

Physics Department, University of Texas at Arlington, Arlington, TX 76019, USA

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Abstract

The computational formalism of the full-potential all-electron linearized augmented plane wave plus local orbitals (FP-LAPW + lo) method has been employed to study the relaxation of the δ-Pu(1 1 1) surface and the consequent effects for atomic adsorption of C, N, and O atoms on this surface. The underlying theoretical principle is the generalized gradient approximation to density functional theory (GGA-DFT) and the surface was modeled by a five-layer slab with a (2×2) surface unit cell. Upon relaxation of the slab, the interlayer separation between the surface and the subsurface layers expanded by 7.1% with respect to the bulk interlayer separation, while the separation between the subsurface and central layers expanded by 0.4%. To study adsorption on the surface, the adatoms were allowed to approach the surface at four high symmetry adsorption sites, namely, the top, bridge, hollow FCC, and hollow HCP sites, the adlayer structure corresponding to a coverage of 0.25 of a monolayer in all cases. The hollow FCC adsorption site was found to be the most stable site for C and N with chemisorption energies of 6.420 and 6.549 eV, respectively, while the hollow HCP adsorption site was found to be the most stable site for O with a chemisorption energy of 7.858 eV. The respective distances of the C, N, and O adatoms from the surface were found to be 1.22, 1.09, and 1.22 Å. The work function and net magnetic moments, respectively, increased and decreased in all cases upon chemisorption compared with the bare δ-Pu(1 1 1) surface. The electronic structure of the interactions between the adsorbates and the substrate is discussed in detail.

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1. Introduction

Considerable theoretical efforts have been devoted in recent years to studying the electronic and geometric structures and related properties of surfaces to high accuracy. One of the many motivations for this burgeoning effort has been a desire to understand the detailed mechanisms that lead to surface corrosion in the presence of environmental gases; a problem that is not only scientifically and technologically challenging but also environmentally important. Such efforts are particularly important for systems like the actinides for which experimental work is relatively difficult to perform due to material problems and toxicity. As is known, the actinides are characterized by a gradual filling of the 5f-electron shell with the degree of localization increasing with the atomic number Z along the last series of the periodic table and the increasing prominence of relativistic effects [1–5]. Narrower 5f bands, with properties intermediate between those of localized 4f and delocalized 3d orbitals, near the Fermi level, compared to 4d and 5d bands in transition elements, is believed to be responsible for the exotic structure of actinides at ambient condition [6,7].

The manmade plutonium metal (Pu) is located at the boundary between the light actinides (Th to Np) consisting of delocalized 5f electrons and the heavy actinides (Am to Lw) consisting of localized 5f electrons [8–13]. The face-centered cubic (FCC) δ-Pu is technologically important because it is highly ductile and this property makes it

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*Corresponding author. Tel.: +1 817 272 2503; fax: +1 817 272 3637.
E-mail address: akr@uta.edu (A.K. Ray).

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convenient for engineering applications [14]. This phase is usually stable in the temperature range 593–736 K; however, it can be stabilized at room temperature by small additions of alloying metals like Al and Ga [15–17]. In spite of detailed studies, δ-Pu is not well understood theoretically. Different theoretical approaches have yielded different degrees of success for δ-Pu [18–44] and we have discussed these in detail in our previously published works [30,40]. The primary focus of this work is to study the relaxation of the most stable δ-Pu surface, namely, the (1 1 1) surface, by representing the surface as a five-layer film and the consequent effects on the electronic and geometric structures of C, N, and O atomic chemisorption on the relaxed surface. This work is thus a natural extension of our previously published work on atomic chemisorption on a three-layer non-relaxed surface. To the best of our knowledge, no such study, experimental or theoretical, on the effects on atomic adsorption due to Pu surface relaxation has, so far, been reported in the literature.

2. Computational methodology

As in our previous works, all calculations have been performed within the generalized gradient approximation to density functional theory (GGA-DFT) with the Perdew–Burke–Ernzerhof (PBE) exchange-correlation functional [45,46]. The Kohn–Sham equations were solved using the full-potential all-electron linear augmented plane wave plus local basis (FP-LAPW + lo) method as implemented in the WIEN2k code [47]. This method makes no shape approximation to the potential or the electron density. Within the FP-LAPW + lo method, the unit cell is divided into non-overlapping muffin tins spheres and an interstitial region. Inside the muffin tin sphere of radius R_{MT}, the wave functions are expanded using radial functions (solution to the radial Schrödinger equation) times spherical harmonics with angular momentum up to $l_{\max}^{\mathrm{wf}} = 10$. Non-spherical contributions to the electron density and potential inside the muffin tin spheres were considered up to $l_{\max}^{\mathrm{pot}} = 6$. APW + lo basis is used to describe all s, p, d, and f ($l = 0$, 1, 2, 3) states and LAPW basis were used for all higher angular momentum states in the expansion of the wave function. Additional local orbitals (lo) were added to the 2s semi-core states of C, N, and O and the 6s, 6p semi-core states of Pu to improve their description. The radii of the muffin tin spheres were $R_{\mathrm{MT}}(\mathrm{C}) = R_{\mathrm{MT}}(\mathrm{N}) = R_{\mathrm{MT}}(\mathrm{O}) = 1.1$ a.u. and $R_{\mathrm{MT}}(\mathrm{Pu}) = 2.13$ a.u. The truncation of the modulus of the reciprocal lattice vector used for the expansion of the wave function in the interstitial region $K_{\max}$, was set to $R_{\mathrm{MT}} \times K_{\max} = 8.88$ for the clean slab ($R_{\mathrm{MT}} \times K_{\max} = 4.59$ for the slab-with-adatom), where R_{MT} denotes the smallest muffin tin radius (this implies that plane waves having kinetic energies up to 17.4 Ry were used). The cutoff for the Fourier series expansion of the electron density and potential in the interstitial region was chosen to be $G_{\max} = 14\,\mathrm{Ry}^{1/2}$. Computations were carried out at the scalar relativistic level, that is, spin–orbit coupling (SOC) effects were neglected. Our recent studies [48] have shown that the inclusion of SOC have negligible effects on the adsorption geometries and lowers the adsorption energies by only 0.05–0.27 eV (1.2–4.26%). Of course, computational costs were also a factor in neglecting SOC.

The δ-Pu(1 1 1) surface is modeled by a periodic slab consisting of a (2×2) surface unit cell with five atomic layers and four atoms per layer and a vacuum region of 30 a.u. thickness. Recent GGA-DFT calculations on bulk and (1 1 1) surfaces of δ-Pu have shown that the lowest energy configurations correspond to anti-ferromagnetic (AFM) arrangement of electron spins [40]. Thus, we have used an AFM configuration for our surface which consist of alternating ferromagnetic layers of up- or down-spin atoms along the *c*-axis. Integrations in the Brillouin zone (BZ) have been performed using the special k-points sampling method with the temperature broadening of the Fermi surface by the Fermi distribution where a broadening parameter of 0.005 Ry has been used. This scheme avoids the instability originating from level crossings in the vicinity of the Fermi surface in metallic systems and also reduces the number of *k*-points necessary to calculate the total energy of metallic systems [45,49]. For the present work, a *k*-point grid of $5 \times 5 \times 1$ (13 *k*-points in the irreducible part of the BZ) turned out to be sufficient. *Before relaxation*, the surfaces were constructed using the optimized AFM bulk theoretical lattice constant of $a = 8.55$ Bohr [48]. To relax the slab, the central layer was fixed and the two outermost layers were allowed to relax. A damped Newtonian dynamics scheme was used to optimize the interlayer distances d_{12} and d_{23} and relaxation was performed until the maximum force on each atom was lower than 5.7 mRy/a.u.

To study adsorption on the Pu surface, the adatom, corresponding to a surface coverage of 0.25 ML (monolayer), was allowed to approach the relaxed surface perpendicularly from both sides of the slab to preserve inversion symmetry. The adsorptions sites (shown in Fig. 1) considered were: (i) top site (adatom is directly on top of a Pu atom); (ii) bridge site (adatom is placed in the middle of two nearest neighbor Pu atoms); (iii) hollow HCP site (adatom sees a Pu atom located on the layer directly below the surface); and (iv) hollow FCC site (adatom sees a Pu atom two layers below the surface). The chemisorption energy E_{C} is optimized with respect to the perpendicular distance r_{d} of the adatom from the surface. The chemisorption energy E_{C} is given by

$$E_{\mathrm{C}}(r_{\mathrm{d}}) = \tfrac{1}{2}[E(\mathrm{Pu}) + 2E(\mathrm{X}) - E(\mathrm{Pu} + \mathrm{X})],$$

where $E(\mathrm{Pu})$ is the total energy of the clean relaxed Pu slab, $E(\mathrm{X})$ is the total energy of the isolated adatom, and $E(\mathrm{Pu} + \mathrm{X})$ is the total energy of the Pu slab with the adatom. Thus, $E_{\mathrm{C}} > 0$ implies chemisorption and $E_{\mathrm{C}} < 0$ implies otherwise. To calculate the total energy of the adatom, the isolated atom was simulated in a large box of

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