Understanding oxygen adsorption on 9.375 at. % Ga-stabilized δ -Pu (111) surface: A DFT study

Sarah C. Hernandez,^{a*} Marianne P. Wilkerson,^b and Muhammad N. Huda^c

^aMaterials Science and Technology Division, Los Alamos National Laboratory, Los Alamos, NM
87545

^bChemistry Division, Los Alamos National Laboratory, Los Alamos, NM 87545

^cPhysics Department, University of Texas at Arlington, Arlington, TX 76019

*hernansc@lanl.gov

Abstract

Plutonium (Pu) metal reacts rapidly in the presence of oxygen (O), resulting in an oxide layer that will eventually have an olive green rust appearance over time. Recent experimental work suggested that the incorporation of gallium (Ga) as an alloying impurity to stabilize the highly symmetric high temperature δ -phase lattice may also provide resistance against corrosion/oxidation of plutonium. In this paper, we model a 9.375 at. % Ga stabilized δ -Pu (111) surface and investigated adsorption of atomic O using all-electron density functional theory. Key findings revealed that the O bonded strongly to a Pu-rich threefold hollow fcc site with a chemisorption energy of -5.06 eV. Migration of the O atom to a Pu-rich environment was also highly sensitive to the surface chemistry of the Pu-Ga surface; when the initial on-surface O adsorption site included a bond to a nearest neighboring Ga atom, the O atom relaxed to a Ga deficient environment, thus affirming the O preference for Pu. Only one calculated final on-surface O adsorption site included a Ga-O bond, but this chemisorption energy was energetically unfavorable. Chemisorption energies for interstitial adsorption sites that included a Pu or Pu-Ga environment suggested that over-coordination of the O atom is energetically unfavorable as well. Electronic structure properties of the on-surface sites illustrated by the partial density of states implied that the Ga $4p$ states indirectly influenced the Pu $6d$ states strongly to hybridize with the O $2p$ states, while also weakly influenced the Pu $5f$ states to hybridize with the O $2p$ states, even when Ga was not participating in bonding with O.

Keywords: Density functional theory; plutonium-gallium; surface; oxygen; oxidation; electronic structure

I. Introduction

Due to plutonium (Pu) being oxophilic in nature, the metal is known to be extremely reactive with environmental gases [1,2]. In particular, the high-temperature phase, the δ -phase, is highly susceptible to oxidation. Unlike the brittle α -phase (monoclinic crystal), the δ -phase is ideal for technological applications due to its malleability and ductile properties and is a highly symmetric face-centered-cubic (fcc) crystal structure. The δ -phase exists at 593-736 K, but may be stabilized to room temperature when Pu is alloyed with a number of elements, including gallium (Ga) or aluminum [3]. The inclusion of an alloying impurity may either enhance or hinder the corrosion rate of δ -Pu depending on the atmospheric environment when compared to unalloyed α -Pu [1,2,4]. Haschke et al. [2] reported that in dry air the rate of corrosion between α -Pu and Ga-stabilized δ -Pu was the same, but in moist air or a moist inert environment the rate of corrosion in Ga-stabilized δ -Pu significantly changed. In moist air, α -Pu corroded at a rate of 2.6 nm/hr, while Ga-stabilized δ -Pu corrosion rate was 1.5 nm/hr [4], thus indicating that the inclusion of Ga made δ -Pu corrosion resistant, when compared to unalloyed α -Pu. On the other hand, in an inert moist environment, the rate of corrosion for α -Pu became 16 nm/hr, while Ga-stabilized δ -Pu was 105 nm/hr [4], which indicated that in this particular environment Ga increased the corrosion rate of δ -Pu. In addition, when comparing the high temperature unalloyed δ -Pu to Ga-alloyed δ -Pu the corrosion rate was significantly higher for unalloyed than alloyed δ -Pu [2], but corrosion/oxidation studies of unalloyed δ -Pu at elevated temperatures are limited. Although the Ga impurity in the δ -Pu lattice is inevitable in experimental studies, many previous theoretical studies have not considered the Ga impurity in δ -Pu surface studies.

Past theoretical works have investigated oxygen (O) adsorption on δ -Pu (111) surface without the presence of impurities [5-9]. Their conclusions showed that the O adatom preferred threefold coordination and that the Pu $6d$ and O $2p$ hybridized [5-8]. Observation of slight mixture of hybridization with the Pu $5f$ states was also noted. Under significant coverage of O,

slight reconstruction of the δ -Pu surface to an α -like surface was observed [9]. The phase transformation of Ga-stabilized δ -phase (≤ 2.5 at. % Ga) to the α -phase has been noted experimentally, which has shown that upon cooling Ga-stabilized δ -Pu will undergo a phase transformation to the α' -phase (an expanded α -Pu unit cell) [10,11]. The effects of the alloying impurity on the formation of oxide layers in Pu have also been noted experimentally, where the presence of additional impurities may change the stoichiometry of the oxide. When Pu metal was exposed to air, a layer of Pu dioxide (PuO_2) will form, with an addition of a sesquioxide (Pu_2O_3) layer at the metal-oxide interface [1,2,12-15]. The formation of Pu_2O_3 has been detected in ultra-high vacuum and/or at high temperatures via auto-reduction of PuO_2 by X-ray photoelectron spectroscopy (XPS) and photoelectron spectroscopy (PES) [13-15]. The historical view of the initial growth of PuO_2 has recently been challenged by Pugmire et al. [16]. They concluded that the growth of PuO_2 may be amorphous because ellipsometry measurements revealed that the optical band gap of the oxide agreed well with an amorphous structure. Furthermore, X-ray diffraction analysis (XRD), which is sensitive to the crystalline long-range lattice, showed only the δ -Pu XRD crystal pattern, while other Pu oxide species were not detected. In context of how impurities may affect the growth of the oxide, Garcia Flores et al. [13] reported that depending on the level of carbon contamination, which may be introduced during the casting process, a sub-stoichiometric Pu oxide ($\text{Pu}_2\text{O}_{3-y}$, $y = 0 - 0.7$) will form. To acquire a more accurate model of the oxidation of Ga-stabilized δ -Pu, the Ga alloy impurity *must* be included in relevant theoretical surface studies.

The inclusion of Ga within the δ -phase has only been modeled within the bulk structure [17-22] to explore the stability of the fcc lattice, location of the Ga, and the effect Ga may have on the electronic and magnetic properties of δ -Pu. We have reported the adsorption of O on a 3.125 at. % Ga stabilized δ -Pu (111) [23], which showed that O preferred to be threefold coordinated in a Pu-environment and Ga does influence the electronic structure of the nearest

neighboring Pu atoms. In this paper we selected a higher concentration of Ga within a δ -Pu (111) matrix. The concentration of Ga, 9.375 at. % Ga, was based on a previous bulk study [22], that consisted of a 32-atom fcc δ -Pu supercell, in which the Ga impurity was added in a substitutional fcc site. This structure yielded concentrations of 3.125 (1 Ga and 31 Pu atoms), 6.25 (2 Ga and 30 Pu atoms), and 9.375 (3 Ga and 29 Pu atoms) at. % Ga, and the preferred location of the Ga was a fourth nearest neighboring distance from each other. The 6.25 at. % Ga concentration was not considered in this study, due to the fact that our focus was to gauge the effect Ga may have on the structural and electronic properties of δ -Pu during adsorption with oxygen. Therefore, the two extremes, lowest and highest concentration of Ga, were chosen for the Pu-Ga surfaces.

II. Computational Method

Density functional theory (DFT) and the all-electron full-potential linearized augmented-plane-wave plus local orbital (FP-L/APW+lo) basis method as implemented within the WIEN2k code was used to carry out the calculations [24]. The Perdew-Burke-Ernzerhof (PBE) formulation of the generalized gradient approximation (GGA) to exchange-correlation functional [25] was also used. In order to describe the *s*, *p*, *d*, and *f* states ($l=0, 1, 2, 3$), APW+lo basis functions were employed, along with the LAPW basis for all other higher orders of angular momentum states up to $l_{wf}^{max} = 10$ in the expansion of the wave functions. Local orbitals (LO) were added to the Pu 6s and 6p semi-core states.

Parameters used to model the 9.375 at. % Ga stabilized δ -Pu (111) surface came from a recent Pu bulk system [22]. In this work, it was determined that it was more energetically favorable that when more than one Ga atom existed within the fcc crystal the Ga atoms preferred to be at fourth nearest neighboring distance from each other. In order to maintain Ga concentration and the preferred distance of the Ga atoms from each other, a surface geometry of a periodic slab was modeled with a 4 atomic layers unit cell of $p(4 \times 2)$ surface area.

Theoretical studies revealed that a Pu slab with at least 3 atomic layers was sufficient to model the adsorption of impurities [26-28]. Hence, a slab with four atomic layer thickness with 29 Pu atoms and 3 Ga atoms was considered (Figure 1) for this study. One Ga atom was placed in the topmost surface (layer 1), while the other two Ga atoms were in the subsurface layer (layer 3). Other configurations of the placement of the Ga atoms within the surface were also investigated and will be discussed later in the results section. The bulk study yielded a theoretical lattice constant of 4.493 Å, which was used for the theoretical lattice constants for the slab. Application of the lattice parameters were $a = 12.708$ Å and $b = 6.354$ Å and a vacuum region of 15.9 Å in the z-direction yielded $c = 23.710$ Å. The bulk study indicated that regardless of the Ga concentration, the magnetic ground state structure was anti-ferromagnetic, with the exception at the Ga-site (i.e. the Ga atom yielded no magnetic moment). The surface was then modeled with an anti-ferromagnetic (AFM)-like configuration for only the Pu atoms. AFM-like is defined by the fact that the magnetic configuration is no longer a true AFM system since there were an odd number of Pu atoms. The WIEN2k parameters were kept consistent with previous oxygen adsorption studies on a pure Pu surface and a Pu-Ga surface [7,23]. The WIEN2K parameters were a muffin tin radii (RMT) of 1.127 Å, 1.032 Å, and 0.635 Å for Pu, Ga, and O, respectively, and a plane-wave kinetic energy cutoff of $K_{\max}^2 = 163$ eV for the expansion of the wave function within the interstitial region. Due to prior theoretical works [7,22,23] and a k-point convergence test on the surface, a k-point mesh of 2x4x1 and a temperature broadening parameter of $k_B T = 0.068$ eV were chosen. The convergence criteria for the total energy and charge were 1.36×10^{-4} eV and $1 \times 10^{-3} e^-$, respectively. The molecular O₂ total energy, which was used for calculating the adsorption energy, was computed in a 13.23 Å box and at the Γ k-point.

At the scalar relativistic level of theory, full geometry relaxations were performed by minimizing the total energy with respect to the atomic positions at the no-spin-orbit-coupling level of theory (NSOC). When a maximum Hellman-Feynman force on each atom of less than

0.051 eV/Å was achieved, the relaxations were terminated. Using the optimal scalar relativistic geometries, a single-point calculation was performed with the inclusion of spin-orbit-coupling (SOC). Currently WIEN2k does not have the capability to perform a Hellman-Feynman force computation with the inclusion of SOC. Also due to the fact that WIEN2k calculates the partial forces in the self-consistent cycle and only calculates the total force once charge convergence is achieved, inaccuracies may be introduced in the calculation, affecting the structural integrity. Past theoretical studies have shown that the equilibrium scalar relativistic and SOC-inclusive geometries are quite similar [7,30]. SOC interactions were implemented through a second variational scheme using the scalar relativistic eigenstates as a basis with all eigenstates with the inclusion of energies below 61.2 eV [31]. Only the Pu atoms possessed SOC effects.

As shown in Figure 1, the adsorbate may approach a Pu-terminated (Pu-rich) surface or a PuGa-terminated (Pu and Ga present on the topmost layer) surface. A single O adatom on each termination was considered, which resulted in an adsorbate surface coverage of 0.125 ML. The O adsorbate was initially placed at four high-symmetry Pu-terminated adsorption sites: top (onelfold coordination), bridge (twofold coordination), hollow hcp, and hollow fcc (threefold coordination) (Figure 2). These four initial adsorption geometries corresponded to adsorption on the Pu-terminated surface, but due to the presence of Ga located within the subsurface a fifth site was taken into consideration, a hollow hcp over a Ga atom. On the PuGa-terminated surface an addition of four surface sites were considered: top site on a Ga atom (Figure 2a), bridge site between a Pu and a Ga atom (Figure 2b), hollow hcp site coordinated with Pu and Ga atoms (Figure 2c), and hollow fcc site coordinated with Pu and Ga atoms (Figure 2d). Also similar to the Pu-terminated surface, due to Ga within the subsurface a fcc site over a Ga atom was also included. Octahedral and tetrahedral interstitial sites were also explored, which included interstitials sites that were either in a Pu-rich or Pu-Ga environment (Figure 3). Lastly, *chemisorption energy* is given by $E_c = E_{\text{PuGa+O}} - E_{\text{PuGa}} - \frac{1}{2}E_{\text{O}_2}$, where $E_{\text{PuGa+O}}$ is the total energy

of the Pu-Ga surface with O adatom after relaxation, E_{PuGa} is the total energy of the relaxed bare Pu-Ga surface with no adsorbate, and E_{O_2} is the total energy of the O_2 molecule. Therefore, if $E_c < 0$, then binding is favorable, but otherwise it is unfavorable. We also reported *relaxation energy*, E_r , which is defined as $E_r = E_{\text{relax}} - E_{\text{unrelax}}$. Here, E_{relax} is the total energy of the fully relaxed slab-adsorbate geometry (no constraints) and E_{unrelax} is the total energy of the slab-adsorbate geometry where only the adsorbate was allowed to relax and the slab atomic positions were constrained.

III. Results and Discussions

We commence our results and discussion on the relaxation of the bare Pu-Ga surface, which yielded $\Delta d_{12}/d_o = -4.4\%$, $\Delta d_{23}/d_o = -2.8\%$, and $\Delta d_{34}/d_o = -2.7\%$, where d_o is the bulk optimized interlayer distance and Δd_{ij} is the interlayer separation between layer i and layer j (the topmost layer is layer 1). One Ga atom was incorporated in the d_1 layer and two Ga atoms were incorporated in the d_3 layer. Minor local lateral distortions were observed (~ 0.009 Å) after relaxation and all Ga atoms remained within in the plane of their respective layer. Comparison of the bare Pu-Ga surface to the previous 9.375 at.% Ga bulk results [22] revealed that the local distortion induced by the Ga atom was similar. Table I shows the structural analysis between the bulk and surface. The calculation of the ratio between the relaxed bond lengths to the unrelaxed bond lengths of the Pu-Ga and Pu-Pu bond lengths in the first nearest neighbor shell around the Ga ($d_{\text{relax}}/d_{\text{fcc}}$) yielded an average of 0.985 and 0.983, respectively. The calculated ratios for Pu-Ga and Pu-Pu bond lengths in the bulk were 0.993 and 0.996, respectively. The average bond length contraction was larger in the surface than in the bulk. Analysis of the bulk Pu-Ga bond lengths yielded an average Pu-Ga and Pu-Pu bond contractions of 0.022 Å and 0.013 Å, respectively, whereas the corresponding bond contractions on the surface were 0.049 Å (Pu-Ga bonds) and 0.036 Å (Pu-Pu bonds). Short-range disorder was observed on the surface and was more so than the bulk counterpart. The Pu-Ga and Pu-Pu normalized bond

length standard deviations, which is a measurement of structural disorder, for the surface was 0.019 and 0.042, respectively. In the bulk the standard deviations were 0.012 (Pu-Ga bonds) and 0.010 (Pu-Pu bonds). Like the bulk, the surface retained the overall crystal structure, while compensating the structural disorder. These collective results show that the 9.375 at.% Ga surface was structurally more stable than the 3.125 at. % Ga surface; the ratios of the Pu-Ga and Pu-Pu bonds between the relaxed and unrelaxed structure were lower and the bond length contractions in the 3.125 at. % Ga surface were higher than the corresponding values calculated for the 9.375 at.% Ga surface [23].

The structural stabilities of 3.125 and 9.375 at. % Ga concentration surfaces may be described by the surface relaxation energy, formation energy, and surface energy. These energies for the 3.125 at. % Ga have been reported in Ref. 23. *Surface relaxation energy*, is the total energy of the slab with the atoms fixed at their bulk terminated position minus the total energy after geometry relaxation. For the 9.375 at. % Ga slab surface relaxation energy yielded 0.12 eV/Ga-atom. In comparison, the 3.125 at. % Ga surface relaxation was 0.19 eV/Ga-atom [23]. A similar effect was found in the bulk Ga stabilized δ -Pu, where the relaxation energy dropped from 0.14 eV/Ga-atom to 0.05 eV/Ga-atom for the 3.125 and 9.375 at. % Ga concentrations, respectively [22]. This decrease in surface relaxation energy from the lower to the higher Ga concentrated surface suggested that Ga provides the same stabilizing effect on the surface by retaining the symmetry of the (111) surface. These observations regarding the effects of Ga on surface relaxations cannot be fully validated since there are currently no experimental data in the literature on the relaxation of Ga-stabilized δ -Pu metal surfaces. We recently reported that the formation energy of different Ga concentrated surfaces decreased from 0.36 eV to 0.27 eV as the Ga concentration increased [23]. The positive formation energy indicates the surface is energetically unfavorable, but this is due to the fact that it is unphysical to have a free floating surface. The decrease in formation energy with increasing Ga

concentrations indicated that the surface was becoming more energetically favorable. This trend was also similar to the bulk formation energies, which were -0.028 eV/atom to -0.099 eV/atom with increasing Ga concentrations [22]. In addition, we reported that the surface energy decreased from 1.24 J/m² to 1.19 J/m² with increasing Ga concentration [23]. The inclusion of Ga not only is shown to stabilize the bulk, but also Ga will stabilize the δ -Pu surface.

A. O adsorption and structural geometry analysis

1. *O approaching Pu-terminated surface*

Table II shows the results of O adsorbed on the Pu-terminated surface, and includes the relaxation energies (E_r), chemisorption energies (E_c) at the NSOC and SOC levels of theory, the optimized perpendicular distance of the adsorbate from the surface, and the nearest neighbor distances of the O adatom from the surface atoms. “Site over atom” is defined as the O atom is situated over either a Pu or Ga atom that is located within the subsurface, as discussed in the computational section of this paper.

The least energetically favorable site was the top site with SOC E_c of -3.33 eV; which has also been reported in previous works [7,8,23]. . This value is 0.22 eV greater than the SOC E_c of the 3.125 at. % Ga surface top site O adsorption [23]. The most energetically favorable site was the fcc over a Pu atom site with SOC E_c of -5.06 eV. The experimental standard free energy of formation per oxygen atom for PuO₂ is -5.21 eV (-120.2 kcal/mol) [32]. The discrepancy between the two energies is that within the PuO₂ unit cell, O is coordinated with four Pu atoms, while when it is chemisorbed onto the surface O is coordinated with three Pu atoms. There was only a slight increase by 0.03-0.16 eV in E_c from NSOC to SOC, supporting previous reports that equilibrium scalar relativistic and SOC-inclusive geometries are quite similar [7,30]. The O atom remained at the initial sites for the top, hcp over Pu, hcp over Ga, and fcc over Pu sites, while distorting the local environment. The local distortion can be observed by the sites that have relaxation energy of approximately -1 eV (hcp over Pu, fcc, and bridge sites). Unlike the

3.125 at. % Ga surface, in which the O adatom moved from initial bridge site to a final fcc site [23], the final site of the O adatom for the 9.375 at. % Ga surface bridge site was fourfold coordinated. In contrast to the 3.125 at. % Ga surface, the bridge site did not help mediate the O atom to the lowest energetically hollow site, but rather oxygen-induced distortions were detected in the final geometry for the 9.375 at. % Ga surface. The bond length of the atoms that formed the bridge site expanded from 3.18 Å to 3.79 Å and contractions in all interlayer spacings were noted. This expansion in the bridge site was 0.25 Å greater than the expansion of the bridge site seen in the 3.125 at. % Ga surface. As seen in our previous work for O adsorption on the 3.125 at. % Ga surface [23], oxygen induced distortions were noted and have also been seen from the recent work of Taylor [9]. However, the amount of distortion on the 0.125 ML material did not approach an α -phase as reported for the higher adsorbate coverage reported by Taylor. Note that although oxygen-induced distortions were observed, there was no apparent reconstruction of the surface. The distortions were local around the O adatom. The final distance between the adatom and the slab was 0.97 Å for the bridge-to-fourfold site, resulting in an average neighboring Pu-O bond length of 2.41 Å. The O adatom was closer to the slab and Pu-O bond lengths were longer than the 3.125 at. % Ga results, which had a final distance of 1.11 Å and an average Pu-O bond length of 2.25 Å [23]. We note that the Pu-O bond length in bulk PuO₂ is 2.36 Å. In comparison to the 3.125 at. % Ga results, we saw that the final distance of the O adatom from the surface was the same for the top site (1.86 Å), but distances decreased for all other similar sites (i.e. hcp over Pu, fcc, and bridge sites). All distances of the O atom from the surface were lower than those reported in previous published adsorption studies [7], similar to the O adsorption study for 3.125 at. % Ga surface [23], with the exception of the top site. These results show that, in order to achieve an appropriate description of the distance of the O adatom from the slab and any structural distortions that may be present,

constrained-free atomic relaxations are *necessary* to accurately describe the adsorption geometries.

The hcp over Ga site yielded a chemisorption energy that was the least energetically favorable of the hollow sites and the distance of the O adatom from the surface was greater than all other hollow sites (1.38 Å). The average Pu-O nearest neighboring bond lengths also increased slightly for the hcp over Ga site in comparison to the other hollow sites, from 2.25 Å to 2.27 Å. The chemisorption energy difference between the two different hcp sites was 0.20 eV; thus the presence of Ga in the second layer within the slab from the O adatom affected the favorability of O adsorption on the Pu surface. Even though the local coordination environment of the O adatom was Pu-rich, the increase in chemisorption energy and the significant distance of the O adatom from the surface is indicative of Ga hindering the reaction of O adsorbing onto the Pu surface. The effects of Ga will be elucidated more in the following section.

2. *O approaching PuGa-terminated surface*

Table III shows the results for O adsorbed on the PuGa-terminated surface. When the O is approaching this surface, the Ga is located on the topmost surface and two Ga atoms are located in the third subsurface layer. Configurations of O bonding to Pu and Ga are given in Figure 2. Note that in Table III, we have adopted the nomenclature of site-Pu, site-Ga, or site-PuGa, thus indicating whether the initial site has Pu, Ga, or both (PuGa) atoms as coordination atoms to the O atom. The final site will also make this distinction.

The least energetically favorable site was the top-Ga site, which had an SOC E_c of -1.64 eV and the longest distance from the slab of 1.82 Å for all O final sites on the PuGa-terminated surface. The most energetically favorable site was the hcp-PuGa-to-fcc-Pu site. This site had SOC E_c of -5.01 eV and a distance from the slab of 1.02 Å, which was slightly more in energy than the Pu-terminated fcc adsorption site (energy difference of 0.05 eV). An increase of chemisorption energies from the NSOC to SOC level of theory for all sites was also observed.

The hcp-Pu and bridge-Pu sites yielded lower chemisorption energies compared to similar sites on the Pu-terminated surface, while the fcc-Pu was slightly higher in energy than the Pu-terminated fcc site. When the O adatom was placed on the top site for the Pu-terminated surface, the O remained at the top site, whereas for the PuGa-terminated top-Pu site the O adatom migrated to a final fcc-Pu site, which decreased the chemisorption energy significantly. The chemisorption energy difference between these two top sites was 1.63 eV. The migration of O from a top site to a hollow fcc site had a relaxation energy of -2.09 eV, which is significantly greater in magnitude than the Pu-terminated top site relaxation energy of -0.48 eV, which implies the significant amount of energy for O to migrate to a more energetically favorable site on the PuGa-terminated site. Thus, the presence of Ga on the topmost surface (nearest neighboring atom to the top-Pu site) and within the subsurface enabled the O atom to relax from the top-Pu site to a final fcc-Pu site over a Pu atom in the subsurface, which was not observed in the 3.125 at. % Ga surface adsorption results either [23]. This indicates that the O atom had an affinity to a Pu-rich environment. Additionally by observing the last column in Table III, only the top-Ga site had the final site where the O adatom remained coordinated with a Ga atom, which was not energetically favorable (SOC E_c was -1.64 eV). In all other final sites, the O adatom relaxed to a Pu-rich environment, regardless if a Ga atom was initially coordinated with O. The relaxation energy that was obtained for these sites (hcp-PuGa, fcc-PuGa, and bridge-PuGa) was on average -1.75 eV, which is more than twice the average relaxation energy (-0.84 eV) observed for similar sites (hcp over Pu/Ga, fcc, and bridge) on the Pu-terminated surface. Also local surface distortions due to the O migration was observed within the surface. This migration was not seen in the 3.125 at. % Ga results, where it was observed that the O atom remained coordinated with a Ga atom in all final sites when it was initially placed in a Pu-Ga environment. The 3.125 at. % Ga surface only had one Ga atom located in the topmost surface, whereas for the 9.375 at. % Ga surface the presence of additional Ga atoms within the

subsurface influenced the surface chemistry, which then subsequently affected the final position of the O atom. Also, with the exception of the fcc-Pu over Ga site, all distances of the O atom from the surface were larger than the distances on the Pu-terminated surface by an average of 0.15 Å.

To further probe the influence of the subsurface Ga atoms on surface reactivity, the location of the Ga atoms within two subsurface models were investigated. Figure 4 illustrates the arrangements of these two different Ga subsurface arrangements. Since the most energetically favorable site was the hcp-PuGa-to-fcc-Pu site, for the surfaces shown in Figure 4 we only computed the O adatom placed initially at the hcp-PuGa site only. For the surface in Figure 4a, two possible hcp-PuGa sites were possible in which was the O atom placed over either a Pu or Ga atom located in the subsurface. The SOC chemisorption energies and final sites are shown in Table IV. When the O atom is initially placed in a Pu-Ga coordinated environment along with being located over a Ga atom in the subsurface, the chemisorption energy was less favorable and the O atom was not able to migrate to a Pu-rich environment. On the other hand, when the O atom was located over a Pu atom in the subsurface and the Ga atoms were either in the second or third layer, the O atom was able to relax to a Pu-rich environment and these chemisorption energies were more energetically favorable. The Ga atoms located in the third layer was slightly more energetically favorable by 0.04 eV than when the Ga atoms were located in the second layer. The fourth case, where the Ga atoms are located in the fourth layer, the O atom remained in its initial site and the chemisorption energy was not as favorable. These results concluded that the location of the Ga atoms within the surface and subsurface is decisive on determining the migration of the O adatom to a Pu-rich environment. Lastly, this effect of O migrating to a Pu-rich region can be explained by the dimer formation energy, which was discussed in our previous work [23]. We claim that the order of binding energies stability for the dimers were $\text{Pu-O} > \text{Ga-O} > \text{Pu-Ga} > \text{Pu-Pu}$ and due to the fact that Pu is more

electropositive than Ga, the Pu-O bond is relatively stronger than the Ga-O bond. To summarize, the results above indicate that with the presence of more Ga within the δ -Pu surface matrix, O will migrate to a energetically favorable Pu-rich environment while inducing noticeable relaxation and local distortion of the surface.

3. *Interstitial adsorption*

Table V shows the results for O interstitial adsorption sites. Note that site-1 is Ga not coordinated to O, and site-2 is Ga is coordinated to the O (Figure 3). Structural deformations of the O adatom in an interstitial site were manifested by expansions of the Pu-O and Ga-O bond lengths, which were initially 2.25 Å and 1.95 Å for the octahedral and tetrahedral sites, respectively. Final bond lengths were in the range of 2.32 Å to 2.57 Å and 2.16 Å to 2.27 Å for the octahedral and tetrahedral sites, respectively. Also the final interstitial adsorption sites were distorted. The tetrahedral sites angles had percent errors of 0.40% to 13.28% and the octahedral sites angles had percent errors of 0.38% to 13.79%, and from this we can conclude that the distortion observed for the tetrahedral and octahedral sites were similar. The tetrahedral-2 adsorption site had a final site that was fourfold coordinated, which was a highly distorted tetrahedral site with angles ranging from 95° to 121°. This site differed from the final sites that were fourfold coordinated for the on-surface adsorption results, which were in-plane to the topmost surface and angles differ significantly from a tetrahedral configuration of 109.5°.

The E_c indicated that, regardless of whether O is in a Pu-rich or Pu-Ga region, the E_c were not as energetically favorable as to the on-surface E_c results. O prefers to be threefold on-surface coordinated, likewise seen in previous works [6-8,23]. When the results were compared to similar interstitial sites in the 3.125 at. % Ga surface, the E_c for the 9.375 at. % Ga surface have significantly increased. The Pu-rich environment for the octahedral-1 and tetrahedral-1 sites for the 9.375 at. % Ga surface yielded SOC E_c of -4.22 eV and -4.02 eV, respectively, whereas similar sites for the 3.125 at. % Ga surface were -4.55 eV and -4.64 eV, respectively.

For the Pu-Ga interstitial environment, the octahedral-2 and tetrahedral-2 sites SOC E_c were -3.54 eV and -3.12 eV, respectively, for the 9.375 at. % Ga surface, and similar sites in the 3.125 at. % Ga surface yielded SOC E_c of -4.02 eV for both Pu-Ga interstitial sites. These results show that for the 9.375 at. % Ga surface the degree of least favorability of interstitial adsorption is more evident than the O interstitial adsorption on 3.125 at. % Ga surface. Thus, the presence of additional Ga within the subsurface discourages formation of a subsurface oxide, concluding that for the Pu-Ga surface O adsorption prefers to be an on-surface phenomena.

Computation of a simple Boltzmann distribution of the O adatom within different adsorption sites, which was defined as $P[E_i]/P[E_{i+1}] = e^{(E_i - E_{i+1})/k_B T}$, where E_i denotes the chemisorption energy at adsorption site i , and the progression of i was determined by most to least energetically favorable SOC chemisorption energy, helped further established the preferability of O to on-surface adsorption. In the Boltzmann distribution, we assumed that $T = 300$ K. The Boltzmann distribution provided the probabilities of on-surface versus subsurface adsorption. As the O adatom was approaching the Pu-terminated surface, i_1 was the fcc site (-5.06 eV), i_2 was the hcp over Pu site (-4.74 eV), and the first interstitial site was i_5 , the octahedral-1 site (-4.22 eV). We found that the Pu-terminated on-surface adsorption probability was 99%, whereas for the PuGa-terminated on-surface adsorption probability was 82%. These probabilities differed from the 3.125 at. % Ga on-surface adsorption probabilities, which were 93% for the Pu-terminated and 99% for the PuGa-terminated surface [23]. These probabilities indicated that, for the 3.125 at. % Ga probabilities, the Pu-terminated surface had more potential to have O diffusion into the subsurface, but only if O overcame the potential barrier, and the majority of O would be adsorb on the PuGa-terminated surface. In comparison, the probability of on-surface adsorption of the 9.375 at. % Ga system increased for the Pu-terminated surface, while the PuGa-terminated surface probability decreased in the 9.375 at. % system. These results implied that when the O adatom is approaching the Pu-terminated surface, Ga enhanced the ability of the adsorption to

remain on-surface. For the PuGa-terminated surface, the presence of Ga on the topmost surface and on the third layer from the adatom, allowed the adatom to migrate from a Pu-Ga environment to a Pu-rich environment on the surface, which was not seen in the 3.125 at. % Ga adsorption results. Also since the next subsurface layer was all Pu atoms, the ability of O to diffuse in the subsurface becomes slightly more possible than the PuGa-terminated results from the 3.125 at. % Ga case. The inhibition of O diffusion into the subsurface might be achieved with the presence of Ga being in subsequential layers from the reactive topmost layer. Either way the high probabilities indicate that O diffusion is an activated process, in which significant amount of O dosing would be needed, and that the surface chemistry of the Pu-Ga surface can greatly influence the adsorption of O on the surface, even at these low atomic concentrations of Ga.

B. Electronic structure analysis

Analyses of the partial density of states (PDOS) provides a way to probe the effects of the adsorption of O on the electronic structure of the Pu-Ga surface. In this section, we report the PDOS on adsorption sites that were the least and most preferred sites for both the Pu-terminated and PuGa-terminated surfaces. In Figure 5, PDOS are shown for the Pu-terminated top and fcc site. Note that the Pu bare (Ga bare) are the Pu (Ga) atoms PDOS before adsorption, and Pu+O (Ga+O) are the Pu (Ga) atoms PDOS after adsorption with O. Only atoms coordinated with O are plotted. The PDOS for the top site (Figure 5a) showed that the Pu *5f* states are slightly shifted below the Fermi energy from the Pu bare *5f* states. The Pu *6d* states are hybridizing with the O *2p*, while splitting of the O *2p* states into sub-bands are noted. The Pu-terminated fcc site PDOS (Figure 5b) reveal that the O *2p* states have shifted to lower energies compared to the O *2p* states in Figure 5a and there is a decrease in intensities of the Pu *5f* and *6d* states in comparison to the intensities of the Pu bare states. Hybridization with the O *2p* states is observed. Similarly we see the O *2p* states splitting into sub-bands as seen in

the top site. The spectra of the fcc to fcc site in Figure 5b reveals a decrease in the intensities of the Pu *5f* and *6d* states at the Fermi level compared to the Pu bare spectrum. The trend in which the energies of the O *2p* states decreased with an increased in chemisorption energy is in good agreement with previous work [7,8,23]. The splitting feature of the O *2p* states observed in Figure 5 is also featured in the 3.125 at. % Ga adsorption results, but in the latter case, these features were observed only when the O adatom was adsorbed on the PuGa-terminated surface [23]. Therefore, the increase of Ga atoms in the 9.375 at. % Ga surface likely allowed for the Pu *6d* states to more readily participate in bonding through an indirect influence from the Ga. This phenomenon was shown in the previous bulk results [22], which indicated that with increasing Ga concentrations, the energy of the Pu *6d* states decreased in magnitude, while hybridizing with the Ga *4p* electrons. Even though Ga was not present in the Pu-terminated surface, the Pu atoms that are coordinated with the O are within nearest neighboring distance to a Ga atom that was located in the sub-surface. In summary, the PDOS illustrated in Figure 5 indicated that the presence of Ga as a nearest neighboring atom to the Pu atoms on the topmost surface allowed the Pu atoms to more readily hybridize with O, as observed in the hybridization between Pu *6d* and O *2p* states.

The top-Ga site (Figure 6a) PDOS showed strong hybridization of the Ga *4s* and *4p* states with the O *2p* states, and a decrease in intensity at the Fermi level for the Ga *4p* states. These features are similar to the features observed for the top-Ga site for the 3.125 at. % Ga results. For the most favorable site, hcp-PuGa-to-fcc-Pu, PDOS (Figure 6b) depicted that the O *2p* states hybridized with the Pu *5f* and *6d* states, with a reduction of intensity observed in the Pu *5f* and *6d* states. These features were not observed in the 3.125 at. % Ga results, in which the Pu *5f* states retained the degree of intensity when compared to the bare Pu electronic states, which suggested that the Ga was suppressing the Pu *5f* electrons to hybridize with the O [23]. This claim cannot be concluded for the PuGa-terminated surface results in this work, but

the presence of Ga enhanced the ability of the Pu $6d$ to hybridize with the O $2p$, in addition to affecting the $5f$ electrons indirectly (*vide supra*). To further explain this phenomenon, previous theoretical studies of bulk Pu (no Ga present) indicated there was strongly hybridized d - f character [33]. It has also been postulated that, with the inclusion of Ga within the δ -Pu bulk structure, the “stabilization mechanism” of δ -Pu to room-temperature is provided by the fact that the presence of Ga tends to shift the Fermi level in such a way that decreases the f -bonding nature, subsequently enhancing the d -bonding characteristics [34]. Furthermore, in Pu_3Ga it was observed that there was covalent bonding between Pu d - f and Ga p states [35]. In our previous bulk study, the Pu $5f$ states remained unaffected in the presence of Ga, while the Pu $6d$ states hybridized with Ga $4p$ states with increasing Ga concentrations [22]. However, analysis of the nearest neighboring Ga atom PDOS in conjunction with the PDOS in Figure 6b, revealed that Ga hybridized slightly with the Pu $5f$ electrons near the Fermi level, while strong hybridization with the Pu $6d$ electrons was observed before O was adsorbed (Figure 7). After O absorption the Ga enhanced hybridization between the Pu d -states with the O $2p$ states, while also indirectly affected the Pu $5f$ states to slightly hybridize with the O. The Ga-Pu nearest neighboring distance was 3.18 Å and the Ga-O distance was 4.09 Å. After adsorption we also observed more pronounced hybridization of the Pu $5f$ and $6d$ states with the Ga $4p$ states in the vicinity of the Fermi level. Since 9.375 at. % Ga is on the cusp of the phase diagram boundary for formation of the Pu_3Ga phase [36], we would expect minimal hybridization of the Pu $5f$ states with the Ga $4p$ in the Pu-Ga surface. Once O adsorption occurred, this process contributed to hybridization between the Pu $5f$ and the Ga $4p$ states, which in turn indirectly enabled the hybridization of Pu $5f$ with O $2p$. Although the electronic structure of Pu-Ga alloys have given some insights into the stabilization of δ -Pu, other mechanisms have also been postulated via magnetic interactions, where the presence of an alloy impurity offsets the balance between ordered and disordered magnetism [37,38].

The PDOS for the interstitial sites are shown in Figure 8. The most energetically favorable interstitial sites, octahedral-1 and tetrahedral-1, where the O atom is in a Pu-rich environment, did not demonstrate splitting of the O $2p$ states into sub-bands. The PDOS for these two sites are similar to the 3.125 at. % Ga cases in which the O adatom was in a Pu-rich environment [23]; there were similar trends in which the energies of the Pu $5f$ and $6d$ states slightly differed when compared to the energies of the bare Pu $5f$ and $6d$ states. Not shown in Figure 8a was that following adsorption of O to Pu, PDOS illustrated that the Ga $4p$ states of the nearest neighboring Ga atom were *not* hybridizing with the Pu $6d$ at the lower energy region where the O $2p$ states were present, but were hybridizing with Pu $6d$ states at higher energies. Therefore, the indirect influence of Ga on the Pu $6d$ states was not seen here. However, the 3.125 at. % Ga adsorption results, where Ga was coordinated to the O adatom, remained the same for the 9.375 at. % Ga interstitial results. Figure 8b showed that after adsorption, the Pu energies of the $5f$ states remained similar to those of the bare Pu $5f$ states, whereas the Ga $4s$ and $4p$ and Pu $6d$ states hybridized with the O $2p$. Therefore, in the interstitial sites, when a Ga atom was participating in bonding with the O atom, the Pu $5f$ states had little or no interaction with the O $2p$ states, while the Pu $6d$ states slightly hybridized with the O $2p$ states. To summarize, when the O adatom was adsorbed at an on-surface site, the addition of more Ga in the slab enhanced the ability of the Pu $6d$ and partially the Pu $5f$ states to hybridized with the O $2p$ states, which was not observed in the interstitial adsorption sites. In comparison to O adsorption on a pure Pu slab, previous results indicated no splitting of the O $2p$ states into sub-bands, while instead hybridization of the Pu $6d$ and O $2p$ with admixture of Pu $5f$ states and a reduction of the $5f$ PDOS was observed [7].

Representative three-dimensional difference charge density plots of the most favorable site for the Pu-terminated surface (fcc site) and a site where Ga and O are bonded, the tetrahedral-2 site, are shown in Figure 9. The difference charge density was computed as $\Delta n(r) = n(\text{Pu-Ga} +$

$O) - n(\text{Pu-Ga}) - n(\text{O})$, where $n(\text{Pu-Ga} + \text{O})$ is the total charge density of the Pu-Ga system with O adatom, $n(\text{Pu-Ga})$ is the total charge density of the Pu-Ga slab, and $n(\text{O})$ is the charge density of the O atom. A real space picture for assessing the redistribution of electron density after the adsorption process is illustrated in Figure 9. In Figure 9a, electron density accumulation around the O atom (red regions) and electron density depletion around the Pu (blue regions) are elucidated. In Figure 9b, where the O adatom is fourfold coordinated with three Pu atoms and one Ga atom, showed charge accumulation around the O atom while the Pu and Ga atoms are losing charge. To further quantify the charge accumulation of O, calculation of the net valence partial charges, which are calculated within the muffin tin spheres, show that in both systems a net valence charge of 0.20 for the O adatom, thus verifying that the O atom is accumulating charge from its surrounding neighbors. Results of the adsorbate-induced work-function changes with respect to the clean Pu-Ga surface, which is given by $\Delta\phi = \phi^{\text{adatom/PuGa}} - \phi^{\text{PuGa}}$ for the NSOC and SOC level of theory, is shown in Table VI. Changes in the work function may be explained by the fact that O is more electronegative than Pu and Ga, and a partial transfer of electrons from the Pu-Ga surface to the O adsorbate will occur, which subsequently will induce a surface dipole formation. The magnitude of the induced surface dipole moment is proportional to the change in work function [40]. The work function changes for the interstitials sites are not shown, because $\Delta\phi$ was negligible (on the order of 0.01 eV). The least preferred sites, Pu-terminated top site and PuGa-terminated top-Ga site, have the largest change in work function, while the most energetically preferred sites have the lowest change in work function. These trends agreed well with previous works [6-8,23]. Thus, the electron charge transfers illustrated in Figure 9 agreed with the change in the net valence increase for the O adatom and for the adsorbate-induced work-function shifts.

IV. Conclusions

In conclusion, the interactions of atomic O with a Ga stabilized δ -Pu (111) surface were explored. Incorporation of more Ga in the δ -Pu surface was determined to be more stable than either the 3.125 at. % Ga or pure Pu surface, as revealed by the decrease in surface energy, surface relaxation energy, and formation energy. The 9.375 at. % Ga δ -Pu surface also retained the fcc symmetry while introducing short range disorder around the Ga atoms, which were similar to models obtained from a previous bulk study. Key findings indicated that the O preferred a Pu-rich environment, where the fcc site was the most energetically favorable site, supporting a chemisorption energy of -5.06 eV. Additionally, when the O adatom was approaching the PuGa-terminated surface, the O atom migrated to a Pu-rich environment, which was not predicted for a surface with a lower Ga concentration. The inclusion of more Ga at the surface implied that the surface chemistry was extremely important in determining the adsorption of O onto the Pu surface. This was observed by: 1) Binding of Ga-O was not as favorable as Pu-O. 2) Migration of the O adatom on the PuGa-terminated surface to a Pu-rich environment had significant relaxations of the surface compared to similar sites on the Pu-terminated surface. 3) Location of the Ga in the subsurface influenced whether or not O migrated and affected the chemisorption energy. 4) Adsorption probabilities showed that subsurface Ga maintained on-surface adsorption for the Pu-terminated surface, which was further concluded by the energetically unfavorable interstitial adsorption sites.

Electronic properties elucidated that the Ga $4p$ states indirectly influenced the Pu $6d$ to hybridize with the O $2p$ states, inducing the O $2p$ states to split into sub-bands, which were seen in all on-surface PDOS. This result differed from those obtained from the lower concentrated Ga surface, in which the splitting of the sub-bands was only observed on the PuGa-terminated surface. In addition, slight hybridization of the Pu $5f$ with the O $2p$ states was also observed. These effects were not seen in the interstitial sites when the O atom was coordinated to all Pu

atoms. Charge density difference plots showed that O accumulated charge from both the Pu and Ga atoms, due to the high electronegativity of O, and absorbate-induced work function changes verified this charge transfer. Lastly, these results imply that the presence of Ga within the δ -Pu (111) surface will limit the oxidation of δ -Pu.

Acknowledgements

This work was supported by the US Department of Energy through the Los Alamos National Laboratory LDRD Program. Los Alamos National Laboratory is operated by Los Alamos National Security, LLC, for the National Nuclear Security Administration of U.S. Department of Energy (contract DE-AC52-06NA25396). S.C.H. would like to gratefully acknowledge discussions with Raymond Atta-Fynn (UTA), T. J. Venhaus (LANL), and P. Roussel (AWE). Computational support from the Texas Advanced Computing Center (www.tacc.utexas.edu) and the University of Texas at Arlington supercomputing facilities are also gratefully acknowledged.

References

1. J. M. Haschke and T. H. Allen, *J. Alloys and Compounds* **243**, 23-35 (1996).
2. J. M. Haschke, T. H. Allen, and L. A. Morales, *Challenges in Plutonium Science*, Los Alamos Sci. **number 26**, 253 (2000).
3. F. H. Ellinger, C. C. Land, and V. O. Struebing, *J. Nucl. Mater.* **12**, 226-236 (1964).
4. J. B. Raynor and J. F. Sackman, *Plutonium 1965: Proceedings of the 3rd International Congress on Plutonium*, eds. A. E. Kay and M. B. Waldron, 575-591 (1965).
5. M. N. Huda and A. K. Ray, *International Journal of Quantum Chemistry* **105**, 280-291 (2005).
6. M. N. Huda and A. K. Ray, *Eur. Phys. J. B.* **40** 337-346 (2004).
7. R. Atta-Fynn and A. K. Ray, *Phys. Rev. B* **75**, 195112 (2007).
8. R. Atta-Fynn and A. K. Ray, *Physica B* **400**, 307-316 (2007).
9. C. D. Taylor, *Surf. Sci.* **618**, 101 – 108 (2013).
10. A. J. Schwartz, H. Cynn, K. J. M Bloaum, M. A. Wall, K. T. Moore, W. J. Evans, D. L. Farber, J. R. Jeffries, and T. B. Massalski, *Progress in Materials Science* **54**, 909-943 (2009).
11. S. S. Hecker, D. R. Harbur, and T. G. Zocco, *Progress in Materials Science* **49**, 429-485 (2004).

12. D. T. Larson and D. L. Cash, J. Phys. Chem. **73**(9), 2814-2820 (1969).
13. H. G. Garcia Flores, P. Roussel, D. P. Moore, and D. L. Pugmire, Surf. Sci. **605**, 314-320 (2011).
14. A. J. Nelson and P. Roussel, J. Vac. Sci. Technol. A **31**(3), 031406 (2013).
15. M. T. Butterfield, T. Durakiewicz, E. Guzewicz, J. J. Joyce, A. J. Arko, K. S. Graham, D. P. Moore, and L. A. Morales, Surf. Sci. **571**, 74-82 (2004).
16. D. L. Pugmire, H. G. Garcia Flores, Plutonium Futures The Science 2014, Las Vegas, NV, September 7-12, 2014, 355.
17. P. Söderlind and A. Landa, J. Nucl. Mater. **448**, 310-314 (2014).
18. P. Söderlind, A. Landa, J. E. Klepeis, Y. Suzuki, and A. Migliori, Phys. Rev. B **81**, 224110 (2010).
19. G. Robert, A. Pasturel, and B. Siberchicot, J. Alloys and Comps. **444-445**, 191-196 (2007).
20. B. Sadigh and W. G. Wolfer, Phys. Rev. B **72**, 205122-1 – 205122-12 (2005).
21. K. T. Moore, P. Söderlind, A. J. Schwartz, and D. E. Laughlin, Phys. Rev. Lett. **96**, 206402 (2006).
22. S. C. Hernandez, D. S. Schwartz, C. D. Taylor, and A. K. Ray, J. Phys.: Cond. Matt. **26**, 235502 (2014).
23. S. C. Hernandez, T. J. Venhaus, and M. N. Huda, J. Alloys and Compounds **643**, 253-262 (2015).
24. P. Blaha, K. Schwarz, G. K. H. Madsen, D. Kvasnicka, and J. Luitz, *WIEN2k*, Vienna University of Technology, Austria, 2001, www.wien2k.at.
25. J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).
26. H. Gong and A. K. Ray, Mater. Res. Soc. Symp. **893**, 0893-JJ01-08.1 (2006).
27. H. Gong and A. K. Ray, Surf. Sci. **600**, 2231 (2006).
28. A. K. Ray, J. C. Boettger, Phys. Rev. B. **70**, 085418 (2004).
29. K. Momma and F. Izumi, VESTA: a three-dimensional visualization system for electronic and structural analysis, J. Appl. Crystallogr. **41**, 653-658 (2008).
30. X. Wu and A. K. Ray, Phys. Rev. B **72**, 045115 (2005).
31. D. D. Koelling and B. N. Harmon, J. Phys. C **10**, 3107 (1977).
32. J. T. Waber, W. M. Olson, and R. B. Roof Jr., J. Nucl. Mater. **3** No. 2, 201-215 (1961).
33. R. Jullien, E. Galleani d'Agliano, and B. Coqblin, J. Low Temp. Phys. **10**(5/6), 685 (1973); Phys. Rev. B **6**(6), 2139 (1972).
34. J. van Ek, P. A. Sterne, and A. Gonis, Phys. Rev. B **48**, 16280 – 16289 (1993).

35. J. D. Becker, J. M. Wills, L. Cox, and B. R. Cooper, Phys. Rev. B **54**(24), R17265(R) (1996).
36. S. S. Hecker and L. F. Timofeeva, Challenges in Plutonium Science, Los Alamos Sci. **number 26**, 244 (2000).
37. A. Landa, P. Söderlind, and A. Ruban, J. Phys: Condens. Matter **15**, L371-L376 (2003).
38. A. Landa and P. Söderlind, J. Alloys and Compounds **354**, 99-103 (2003).
39. D. P. Moore, A. L. Broach, D. L. Pugmire, H. G. Flores, T. Durakiewicz, J. Joyce, Actinides 2009, July 12-17 2009, San Francisco, CA.
40. A. Soon, M. Todorova, B. Delley, and C. Stampfl, Phys. Rev. B **73**, 165424 (2006).

Table I: Structural analysis of the first nearest neighboring shell around the Ga atom in the 9.375 at. % Ga bulk and surface systems. The division of the bond length distance in the final relaxed structure by the bond length distance of the pristine structure (d_{relax}/d_{fcc}), the standard deviation of the normalized bond lengths (σ), and the average bond length contractions are tabulated. Bulk data was obtained from Reference 22.

System	Bond Length Type	d_{relax}/d_{fcc}	σ	Average Bond length contractions ($\text{\AA}$)
Bulk	Pu-Ga	0.993	0.012	0.022
	Pu-Pu	0.996	0.010	0.013
Surface	Pu-Ga	0.985	0.019	0.049
	Pu-Pu	0.983	0.042	0.036

Table II: Relaxation energy, E_r , chemisorption energy (E_c) at the no-spin-orbital-coupling (NSOC) and spin-orbital-coupling (SOC) level of theory, and distance of the O adatom from the surface (r_{slab-O}) and distance of the adatom to the nearest neighboring Pu atoms (r_{Pu-O}) for the Pu-terminated surface sites.

Pu-terminated		NSOC		SOC	r_{slab-O} ($\text{\AA}$)	r_{Pu-O} ($\text{\AA}$)
Initial site	Final site	E_r (eV)	E_c (eV)	E_c (eV)		
top	top	-0.48	-3.40	-3.33	1.86	1.86
hcp over Pu	hcp	-0.85	-4.90	-4.74	0.93	2.22, 2.25, 2.28
hcp over Ga	hcp	-0.58	-4.57	-4.54	1.38	2.24, 2.28, 2.29
fcc	fcc	-0.99	-5.13	-5.06	0.97	2.23, 2.24, 2.29
bridge	four-fold	-0.94	-4.62	-4.47	0.97	2.21, 2.22, 2.58, 2.62

Table III: Relaxation energy, E_r , chemisorption energy (E_c) at the no-spin-orbital-coupling (NSOC) and spin-orbital-coupling (SOC) level of theory, and distance of the O adatom from the surface (r_{slab-O}) and distance of the adatom to the nearest neighboring atoms (r_{X-O}) where X is the atom that is nearest to the O adatom, for the PuGa-terminated surface sites. In the last column if value is not followed by “(Ga),” the value relates to a Pu atom.

PuGa-terminated		NSOC		SOC	r_{slab-O} (Å)	r_{X-O} (Å)
Initial site	Final site	E_r (eV)	E_c (eV)	E_c (eV)		
top-Pu	fcc-Pu	-2.09	-5.08	-4.96	1.15	2.19, 2.26, 2.34
top-Ga	top-Ga	-0.76	-1.89	-1.64	1.82	1.82(Ga)
hcp-Pu	hcp-Pu	-0.76	-4.90	-4.80	1.15	2.20, 2.26, 2.35
hcp-PuGa	fcc-Pu	-1.80	-5.07	-5.01	1.02	2.18, 2.27, 2.29
fcc-Pu	fcc-Pu	-0.99	-5.02	-4.92	1.07	2.22, 2.23, 2.32
fcc-PuGa	hcp-Pu	-1.54	-4.97	-4.79	1.08	2.16, 2.26, 2.37
fcc-Pu over Ga	fcc-Pu	-0.82	-4.89	-4.76	0.96	2.22, 2.26, 2.27
bridge-Pu	four-fold	-1.04	-4.74	-4.58	1.10	2.21, 2.23, 2.44, 3.00
bridge-PuGa	hcp-Pu	-1.90	-4.90	-4.75	1.12	2.22, 2.26, 2.31

Table IV: Chemisorption energies for when two Ga atoms are located in a different layer.

Location of 2 Ga	Initial Site	Final Site	SOC
			E_c (eV)
2nd-layer	hcp-PuGa over Ga	hcp-PuGa over Ga	-4.16
2nd-layer	hcp-PuGa over Pu	fcc-Pu over Pu	-4.97
3rd-layer	hcp-PuGa over Pu	fcc-Pu over Ga	-5.01
4th-layer	hcp-PuGa over Pu	hcp-PuGa over Pu	-4.26

Table V: Relaxation energy, E_r , chemisorption energy (E_c) at the no-spin-orbital-coupling (NSOC) and spin-orbital-coupling (SOC) level of theory, and distance of the O adatom from the surface (r_{slab-O}) and distance of the adatom to the nearest neighboring atoms (r_{X-O}) where X is the atom that is nearest to the O adatom, for the interstitial adsorption sites. In the last column if value is not followed by “(Ga),” the value relates to a Pu atom.

Interstitials		NSOC		SOC	r_{slab-O} (Å)	r_{X-O} (Å)
Initial site	Final site	E_r (eV)	E_c (eV)	E_c (eV)		
octahedral-1	octahedral*	-0.60	-4.49	-4.22	-1.17	2.34, 2.36, 3x2.44, 2.47
octahedral-2	octahedral*	-0.48	-3.76	-3.54	-3.73	2.32, 2.35, 2x2.36, 2.37, 2.57(Ga)
tetrahedral-1	tetrahedral*	-0.82	-4.26	-4.02	-2.13	2.23, 2x2.25, 2.27
tetrahedral-2	four-fold	-0.68	-3.36	-3.12	-3.24	2.16, 2.17, 2.19, 2.26(Ga)

*Final sites were distorted interstitial sites.

Table VI: Changes in work function, $\Delta\phi$, at the NSOC and SOC levels of theory. The work function for the clean relaxed Pu-Ga slab was 3.32 eV and 3.39 eV, respectively, at the NSOC and SOC level of theory. Experimental work function is 3.2 eV for stabilized δ -Pu [39].

		NSOC	SOC
		$\Delta\phi$	$\Delta\phi$
		(eV)	(eV)
Pu-terminated	top	0.25	0.25
	hcp over Pu	0.07	0.06
	hcp over Ga	0.13	0.13
	fcc over Pu	0.09	0.07
	bridge	0.04	0.05
PuGa-terminated	top-Pu	0.06	0.05
	top-Ga	0.18	0.17
	hcp-Pu	0.11	0.10
	hcp-PuGa	0.09	0.09
	fcc-Pu	0.09	0.09
	fcc-PuGa	0.09	0.08
	fcc over Ga	0.07	0.07
	bridge-Pu	0.08	0.08
	bridge-PuGa	0.12	0.11

Figure 1: 9.375 at. % Ga stabilized δ -Pu surface, with Ga located in the topmost surface and in the subsurface. Pu atoms are yellow and Ga atoms are purple. Visualization from Ref. 29.

Figure 2: Initial sites for oxygen (blue) adsorbate for PuGa-terminated surface. On top of Ga (a), bridge between Pu and Ga (b), and hollow sites, hcp (c) and fcc (d), with Ga as a nearest neighboring atom.

Figure 3: Octahedral interstitials site with oxygen adsorbate far from Ga (a), octahedral-1, and near Ga (b), octahedral-2. Tetrahedral interstitials site with oxygen adsorbate far from Ga (c), tetrahedral-1, and near Ga (d), tetrahedral-2.

Figure 4: Two Ga atoms located in the second layer (a) and fourth layer (b) with respect to the PuGa-terminated surface.

Figure 5: Partial density of states for the SOC level of theory for the least favorable site, top site (a), and most favorable site, fcc site (b), for when the O absorbate is approaching the Pu-terminated surface.

Figure 6: Partial density of states for the SOC level of theory for the least favorable site, top-Ga (a), and most favorable site, hcp-PuGa-to-fcc (b), for when the O absorbate is approaching the PuGa-terminated surface.

Figure 7: Partial density of states for the PuGa-terminated bridge-PuGa to fcc-Pu site before and after O adsorption. The Pu *6d* and Ga *4p* states have been amplified to show features.

Figure 8: Partial density of states for the SOC level of theory for the most favorable interstitial site, tetrahedral-1 and octahedral-1 [(a) and (c), respectively], and least favorable site, tetrahedral-2 and octahedral-2 site [(b) and (d), respectively], for when the O absorbate is initially placed in an interstitial site.

(a)

(b)

Figure 9: Three-dimensional charge density difference, $\Delta n(r)$, for the fcc site (a) for the Pu-terminated surface, and for the interstitial tetrahedral-2 site (b). Only the coordination environment around the O-atom is shown. Regions of red indicate charge accumulation (positive), while regions of blue indicate charge depletion (negative). Isosurface level is 0.0337 e⁻/cubic Å.