Atomic oxygen adsorption on 3.125 at. % Ga stabilized δ -Pu (111) surface

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Abstract

All-electron density functional theory was used to investigate atomic oxygen adsorption on a gallium stabilized δ -plutonium (111) surface. High symmetry on-surface and interstitial adsorption sites, along with local environment (as determined by the absence or presence of gallium) were explored. The calculations comprised full structural relaxations. Spin-orbit-coupling was also taken into account to assess the complexity of adsorbate-substrate interactions. We observed that O adsorbate prefers to bind strongly to a gallium deficient environment, with the most stable site being the three-fold hollow fcc site and associated chemisorption energy of -5.06 eV. The binding energies were least favored when gallium is a nearest neighbor to the O adsorbate, suggesting that the presence of gallium in a plutonium matrix tends to slow down the oxide layer growth. Although the oxygen coordination is the highest in the interstitial sites, the adsorption energy is less favored compared to on-surface adsorption, implying that the diffusion of oxygen from the surface layer into the subsurface layers is an activated process. The adsorption process induced non-trivial deformations of the surface. Additionally, some delocalization of the plutonium *5f* and *6d* partial electron density of states (PDOS) at the Fermi energy was observed. Further analysis in the PDOS indicated that gallium tends to suppress hybridization between the plutonium *5f* and oxygen *2p* orbitals, while the *6d* orbitals hybridized with oxygen *2p* orbitals.

Keywords: Electronic Structure; Density Functional Theory; gallium-stabilized δ -Plutonium; surface; oxygen

I. Introduction

The stabilized highly symmetric face-centered-cubic (fcc) crystal structure of plutonium (Pu), known as the δ -phase, has been observed to be extremely reactive to environmental gases, which may form oxides, hydrides, carbides, etc.^{1,2} One of the many drawbacks of the observed high reactivity of Pu is the possibility of corrosion-assisted transfer of particulates into the biosphere due to reaction with moist air and oxygen (O). This will certainly lead to unacceptable health consequences. Therefore it is of fundamental interest to probe and fully understand the mechanisms that drive this oxidation and/or corrosion of the Pu metal. In addition, this has implications on the safe storage and eventual disposal of Pu-based radioactive waste material. To be more specific, an atomic scale understanding of the initial reactions of Pu metal surfaces exposed to environmental elements provides insight into the reactivity of the Pu surface, and subsequently provides intrinsic details about the formation of the oxide.

It is well known from experiments that oxidation of plutonium metal will passivate the surface by forming a thin oxide layer; however the oxidation kinetics is quite complicated.² These experiments suggest that when Pu metal is exposed to air, it forms a layer of plutonium dioxide (PuO_2) at the air-oxide interface, while a layer of the sesquioxide (Pu_2O_3) will form at the oxide-metal interface. In an ultra-high-vacuum (UHV) environment, Pu undergoes spontaneous auto-reduction of the PuO_2 into the Pu_2O_3 .³ Eventually, PuO_2 will be completely converted to Pu_2O_3 . This suggests that PuO_2 does not coexist with Pu metal thermodynamically.² Recently, Nelson and Roussel⁴ performed UHV experiments that involved dosing of oxygen at low temperatures on a 2.08 atomic (at.) % gallium (Ga) stabilized δ -Pu sample; they observed that a layer of Pu_2O_3 formed rapidly and then was followed by a formation of a PuO_2 layer. Upon heating the sample, the PuO_2 quickly reduces to the Pu_2O_3 . These results were similar to the photoemission spectroscopy studies done by Butterfield et al.,⁵ but the key results from Nelson and Roussel⁴ was that the activation energy for the auto-reduction of PuO_2 to Pu_2O_3 was 38.8 kJ/mol and that

the oxide that was formed at room temperature, x-ray diffraction measurements taken after 40 days from the formation of the oxide indicated that the oxide growth is amorphous. Also the initial growth of the oxide has been observed to be amorphous, thus challenging the historical perspective of the oxide growth.⁶ Finally, the roles of impurities may change the stoichiometry of the oxide. For instance, Garcia Flores et al.³ reported that the level of carbon contamination introduces a sub-stoichiometric Pu oxide ($\text{Pu}_2\text{O}_{3-y}$), therefore challenging the accepted belief of the stoichiometric stability of Pu_2O_3 .

Density functional theory (DFT) provides a mean to explore the interaction of environmental gases with surfaces at an atomic scale. Previous DFT surface studies of oxygen adsorption on the δ -Pu (111) surface have given initial insight into the electronic effects,⁷⁻¹⁰ and more recently the possible reconstruction of the surface.¹¹ To briefly summarize some key findings, molecular oxygen does dissociate as it approaches the Pu surface,⁷ and when the oxygen adatom approaches the surface, it binds to the surface with a three-fold coordination (preferably the hollow hexagonal-closed-pack site) with adsorption energy of ~ 8 eV. This is associated with an increase in work function due to ionic bonding between the Pu and O atom. Also, hybridization of Pu $6d$ and O $2p$ orbitals with some mixture of Pu $5f$ states are noted.⁷⁻¹⁰ In addition, Taylor¹¹ concluded that initial oxidation coverage is a local environmental phenomenon, but at 1.0 monolayer (ML) coverage of oxygen, significant reconstruction of the surface (up to three atomic layers) of a PuO_2 -like structure on the topmost surface was observed. The O atoms were four-fold coordinated with the Pu atoms that had been “lifted” out of the plane of the surface. Although many theoretical studies have investigated pure δ -Pu surfaces, δ -Pu actually exists at room temperature in an alloyed state.¹²⁻¹⁴ The alloying materials include gallium or aluminum. Furthermore, depending on the external environment the Ga impurity can either enhance or hinder the corrosion rate of δ -Pu when compared to unalloyed Pu.^{1,15} Thus, a realistic surface model of δ -Pu at ambient conditions should include the alloy materials at concentrations

consistent with experiment. In this regard, this work will explore the effects of oxygen adsorption on the δ -Pu (111) surface when a Ga impurity is present in the surface. While past theoretical works on the structural and electronic properties of Pu-Ga bulk have been investigated,¹⁶⁻¹⁹ to the best of our knowledge, this is the first theoretical attempt to elucidate the effects of Ga on atomic oxygen interaction with the δ -Pu (111) surface. It is worth mentioning that within the realm of DFT, describing the electronic structure of δ -Pu sufficiently has been problematic. This is due to the strongly-correlated dual delocalized/localized nature of the $5f$ electrons. Theoretical studies that invoke methods beyond DFT (DFT+U, hybrid DFT, and DFT+DMFT) have been explored and a comprehensive summary of these studies have been published by Söderlind et al.,²⁰ but alternative methods are not more efficient and are too expensive to effectively study the Pu surfaces as we intend to do here. Thus in this work, using DFT, we have found that the oxygen atom is three-fold coordinated in a Pu-rich environment. On the other hand, when a Ga atom is present, chemisorption energies are less favorable and the interaction between the Pu and O atoms is reduced.

II. Computational Method

The calculations were performed using 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.²¹ The Perdew-Burke-Ernzerhof (PBE) formulation of the generalized gradient approximation (GGA) to exchange-correlation functional²² was used. APW+lo basis functions was used to describe the s , p , d , and f states ($l=0, 1, 2, 3$), and the LAPW basis is used for all other higher orders of angular momentum states up to $l_{wf}^{max} = 10$ in the expansion of the wave functions. Additional local orbitals (LO) were added to the Pu $6s$ and $6p$ semi-core states.

The 3.125 at. % Ga stabilized δ -Pu (111) surface was modeled based on parameters from a previous bulk study.²³ To maintain a Ga concentration in a surface geometry consistent with the

bulk geometry, a periodic slab model with a $p(4 \times 2)$ surface geometry was employed. Past theoretical studies have shown that a Pu slab with at least 3 atomic layers is sufficient to model the adsorption of impurities.²⁴⁻²⁶ Thus a slab with four atomic layer thickness was employed (cf. Figure 1). The slab contains 31 Pu atoms and 1 Ga atom. The theoretical lattice constant of 4.523 Å obtained from the bulk study was used for the theoretical lattice constants for the slab, yielding lattice parameters of $a = 12.794$ Å and $b = 6.397$ Å. A vacuum region of 15.9 Å was applied to the third dimension, hence $c = 23.710$ Å. The bulk study indicated that with the inclusion of Ga, the ground state structure was anti-ferromagnetic (with the exception at the Ga-site), thus the surface was modeled with an anti-ferromagnetic (AFM)-like configuration for the Pu atoms. AFM-like here implies that the magnetic configuration is not strictly AFM since there are an odd number of Pu atoms. The WIEN2k parameters were kept consistent with previous oxygen adsorption studies.⁹ The parameters comprised 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 in the interstitial region. Due to previous works^{9,23} and a k-point convergence test, a k-point mesh of $2 \times 4 \times 1$ and a temperature broadening parameter of $k_B T = 0.068$ eV was chosen. The convergence criteria were 1.36×10^{-4} eV and 1×10^{-3} e⁻ for the total energy and charge, respectively. The molecular O₂ total energy, which was used for the adsorption energy calculation, was calculated in a 13.23 Å box and at the Γ k-point.

Full geometry relaxations at the scalar relativistic level, no spin-orbit coupling (NSOC), were carried out by minimizing the total energy with respect to the atomic positions. The relaxations were terminated when the maximum Hellman-Feynman force on each atom was less than 0.051 eV/Å. After the scalar relativistic relaxations, a single calculation was performed with the inclusion of spin-orbit-coupling (SOC) using the optimal scalar relativistic geometries. Currently WIEN2k does not have the capability to perform a Hellman-Feynman force computation with the

inclusion of SOC. It should be pointed out that within WIEN2k, the Hellman-Feynman force computation is performed by calculating the partial forces in each self-consistent cycle. Once charge density convergence is reached, calculation of the total forces is then carried out. This method may introduce inaccuracies within the forces, and could therefore affect the integrity of the structural relaxation. Furthermore, prior studies indicate that the equilibrium scalar relativistic and SOC-inclusive geometries are quite similar.^{9,28} SOC interactions were included via a second variational scheme using the scalar relativistic eigenstates as a basis with all eigenstates with energies below 61.2 eV included.²⁹ SOC effects were added only to the Pu atoms.

The effects of Ga on the adsorption mechanisms can be probed by placing Ga on the surface layer (case 1) or subsurface layer (case 2). Our initial assessments indicated that at both the NSOC and SOC levels of theory, the slab total energies for case 1 and case 2 were nearly degenerate. Hence since our focus for this work was to probe the effect that Ga on on-surface adsorption, we found it instructive to consider case 1. Figure 1 depicts the slab model for case 1. From the figure, it is obvious that the adsorbate may approach a Pu-terminated (Pu-rich) surface or a PuGa-terminated surface. In this work, adsorption of a single O adsorbate on each face was considered, resulting in an adsorbate surface coverage of 0.125 ML. The O adsorbate was initially placed at four high-symmetry adsorption sites: top (one-fold coordination), bridge (two-fold coordination), hollow hcp, and hollow fcc (both hollow sites are three-fold coordination). These four initial adsorption geometries correspond to adsorption on the Pu-terminated surface. Due to the presence of Ga, there were eight initial adsorption geometries on the PuGa-terminated surface: all the four sites on the Pu-terminated surface plus top site on Ga, bridge site between a Pu and Ga atom, and two hollow sites that included a Ga atom in the three-fold coordination. Figure 2 depicts the adsorption sites for which the Ga atom is a coordination atom. The subsurface octahedral and tetrahedral interstitials sites were also investigated. Again, due to the presence of Ga, multiple interstitials sites were inspected, which

included interstitials sites that systematically moved away from the Ga impurity within the slab (Figure 3). Finally, *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 clean Pu-Ga surface, and E_{O_2} is the total energy of the O_2 molecule. Therefore, if $E_c < 0$, then binding is favorable, otherwise it is unfavorable.

III. Results and Discussions

Relaxation of the bare Pu-Ga surface (that is, no adsorbate present) yielded $\Delta d_{12}/d_o = -1.1\%$, $\Delta d_{23}/d_o = 3.7\%$, and $\Delta d_{34}/d_o = -3.2\%$, 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). The d_1 layer had the Ga atom and after relaxation the Ga atom remained planar with very small local lateral distortions (~ 0.001 Å). Comparing the PuGa-terminated surface to the previous 3.125 at.% Ga bulk results,²³ we observe that the local distortion induced by Ga is similar. Specifically, the ratio between the relaxed bond lengths to the unrelaxed bond lengths of the Pu-Ga and Pu-Pu bonds in the first nearest neighbor shell around the Ga were 0.977 and 0.982, respectively. For the bulk, both ratios were 0.978. Also, the previous study of bulk Pu-Ga yielded average Pu-Ga and Pu-Pu bond contractions of 0.069 Å, whereas the corresponding bond contractions on the surface were 0.072 Å (Pu-Ga bonds) and 0.059 Å (Pu-Pu bonds). Although a bond length contraction was noticed in both systems, short-range disorder was more prevalent in the surface. This is evidenced by the normalized Pu-Ga and Pu-Pu bond length standard deviations (measurement of structural disorder) of 0.018 and 0.019, respectively, for the surface, whereas little or no deviation was seen in the bulk. The contraction seen in the topmost Pu-rich surface layer is due to the missing neighbors of atoms. Overall, there were little or no lateral relaxations of the Pu-Ga surface.

The *surface relaxation energy*, which is defined as the total energy of the slab with the atoms fixed at their bulk terminated position minus the total energy after geometry relaxation

was 0.19 eV (that is, relaxation of the atomic positions lowers the slab total energy by 0.19 eV). In comparison, the relaxation of a p(4x2) δ -Pu (111) slab (pure Pu slab; no Ga) was also investigated and the total energy was lowered by 0.11 eV. Thus Ga provides the same stabilizing effect on the surface as it does in bulk δ -Pu. Currently, there is no experimental data in the literature on the relaxation of Ga-stabilized δ -Pu metal so the observations regarding the effects of Ga on surface relaxations cannot be fully validated. To further probe the stability of the δ -Pu surface by Ga, we computed the *formation energy* defined as $E_f = E_{slab} - (m/32)*E_{Pu-bulk} - (n/8)*E_{Ga-bulk}$, where E_{slab} was the total energy of the Pu-Ga surface, $E_{Pu-bulk}$ was the total energy of the Pu-bulk, $E_{Ga-bulk}$ is the total energy of the orthorhombic Ga bulk, m is the number of Pu atoms in the surface, and n is the number of Ga atoms in the surface. The computed values of E_f for the 0, 3.125, and 9.375 at. % Pu-Ga surfaces were 0.40 eV, 0.36 eV and 0.27 eV/atom, respectively. Thus the order of decreasing surface stability is 9.375 at. % Ga > 3.125 at. % Ga > Pu. Also, the *surface energy*, defined as $\gamma = [1/(2A)]*[E_{slab} - E_{bulk}]$, where A is the surface area of the slab, E_{slab} is the total energy of the surface, and E_{bulk} is the total energy of the bulk, was computed for each system. The surface energies for the 0, 3.125, and 9.375 at. % Ga surfaces were computed to be 1.24 J/m², 1.23 J/m², and 1.19 J/m², respectively. Again the order of decreasing surface stability is 9.375 at. % Ga > 3.125 at. % Ga > Pu. Collectively, the two trends in E_f and γ further supports our earlier assertion that the inclusion of Ga coupled with increasing Ga concentrations stabilizes the surface.

A. Adsorption energies and geometries

1. Adsorption on Pu-terminated surface

Table I shows the results of the O adsorbed on the Pu-terminated surface. Reported in the Table I is the *relaxation energy*, E_r , defined as $E_r = E_{relax} - E_{unrelax}$. 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 but only the adsorbate was allowed to relax and the slab atomic

positions were constrained. Also reported in Table I are the adsorption energies at the NSOC and SOC levels of theory, optimized perpendicular distance of the adsorbate from the surface, and the nearest neighbor distances of the adsorbate from the surface atoms.

We observe that the top site was the least favorable site, with SOC chemisorption energy of -3.55 eV; which has been seen in previous works.^{9,10} It can also be seen in Table I that the chemisorption energies for hcp, fcc, and bridge-to-fcc sites at the NSOC level differ by a few tenths of an eVs (in the -4.50 eV to -4.90 eV range). With the inclusion of SOC, the chemisorption energies slightly decreased by 0.08-0.15 eV, supporting previous assertions that equilibrium scalar relativistic and SOC-inclusive geometries are quite similar and that SOC energies are slightly more stable than NSOC energies.^{9,28} The most preferred site, after relaxation of the slab indicated that the initial bridge site had a final hollow fcc site, with three-fold coordination and yielded a SOC chemisorption energy of -4.98 eV. This supports the conclusions from Atta-Fynn's and Ray's^{9,10} work that the bridge site will mediate the lowest energy pathway from a stable hollow site to a neighboring hollow site. The final geometry showed that there were oxygen-induced local distortions (Figure 4). The bond length of the atoms forming the bridge site expanded from 3.20 Å to 3.56 Å coupled with contractions in all interlayer spacings. This implies that the bridge-to-fcc site adsorbate configuration is achieved at the expense of introducing local structural distortions on the surface Pu atoms. Such oxygen induced distortions have been seen theoretically from the recent work of Taylor,¹¹ but Taylor's results correspond to high adsorbate coverage (1 ML compared to 0.125 ML in this work). Nevertheless, in order to see amorphous growth of the oxide, higher coverage of O on a larger surface area slab together with molecular dynamics simulations would be required. This is beyond the scope of this work. Experimentally however, the stability of the δ -Pu surface has been noted by Cox,³⁰ which concluded that a 3.40 at. % Ga stabilized δ -Pu surface had an induced surface phase transformation to the α -phase (room temperature phase of Pu), but the

author did not clearly state whether the observed effect was due to sample preparation or the presence of oxygen on the surface. The final distance of the adatom from the slab was 1.11 Å for the bridge-to-fcc site, resulting in an average neighboring Pu-O distance of 2.25 Å. We note that the Pu-O distance in bulk PuO₂ is 2.36 Å. All distances of the O atom from the surface was lower than those reported in previous published works, with the exception of the top site. For example, in Atta-Fynn's and Ray's⁹ work where the atomic positions of the slab atoms were constrained and only the oxygen adsorbate was allowed to relax, the reported distances were 1.84 Å for the top site, and 1.23 Å for the fcc site. Compared to this work, the distances are 1.86 Å for the top site, and 1.07 Å and 1.11 Å for the two different fcc sites. These differences suggest that constrained-free atomic relaxations are necessary to accurately describe the adsorption geometries.

2. Adsorption on PuGa-terminated surface

Table II shows the results for O adsorbed on the PuGa-terminated surface. Note that in Table II, 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 nearest neighboring atoms. The final site does not make this distinction, since the last column indicates the nearest neighboring atoms. It can be clearly seen that the preferred sites are sites that have all Pu atoms as nearest neighboring atoms, with the most favorable site being bridge-Pu-to-fcc site with a SOC chemisorption energy of -5.06 eV. The sites, top-Pu, fcc-Pu, and bridge-Pu, are all comparable in value from similar sites on the Pu-terminated surface. The difference in chemisorption energies ranges from 0.03 to 0.08 eV. The hcp-Pu site has a chemisorption energy difference of 0.18 eV from the hcp site on the Pu-terminated surface; this could be due to the fact that the relaxation energy for the hcp-Pu site for the PuGa-terminated surface yielded -0.55 eV, while the hcp site for the Pu-terminated surface yielded a value of -0.27 eV. Therefore, more relaxation of the PuGa-surface occurred, which could be explained by the misfit Ga atom

present on the surface. Either way, all PuGa-terminated Pu-rich surface sites similar to the Pu-terminated surface sites had equivalent final geometric sites.

We also observe from Table II that the participation of Ga in the adsorption process leads to a decrease in the chemisorption energies near Ga-sites. Thus all sites with a Ga-O bond *are less favorable* compared to Pu-O bond-only sites. The SOC chemisorption energies are -1.62 eV, -3.85 eV, -4.01 eV, and -4.09 eV for the top-Ga, hcp-PuGa, bridge-PuGa, and fcc-PuGa, respectively. Nevertheless, the pattern is similar to the Pu-terminated surface whereas the fcc site is the most favorable site, and this consistent decrease in chemisorption energy implies that oxygen prefers an all Pu atom environment (very little Ga influence). To buttress this point, we carried out dimer formation energy calculations and the order of binding energies stability were Pu-O > Ga-O > Pu-Ga > Pu-Pu. Therefore, the Ga-O bond is relatively weaker than the Pu-O bond, which agrees with our assertions. This may be explained by fact that Pu is more electropositive than Ga.

3. *Interstitial adsorption*

Table III shows the results for the interstitial sites. Note that site-1 is near the Ga, site-2 is in the middle of the four-layers, and site-3 is far away from the Ga (Figure 3). The results demonstrate that even with oxygen in an all Pu environment, the chemisorption energies are still not as favorable as on-surface oxygen adsorption. Thus establishing that O atom prefers a three-fold on-surface coordination environment. The octahedral-1 and tetrahedral-1 sites, where a Ga atom is participating in bonding with the O adatom have the least favorable SOC chemisorption energy of -4.02 eV. In addition to these low chemisorption energies, we also observed that the interlayer separation has an expansion in the d_{12} interlayer as opposed to the contraction seen in the slab with no O adsorbate. There is also a decrease in expansion in the d_{23} interlayer and increase in contraction in the d_{34} interlayer. The most favorable SOC chemisorption energy of -4.64 eV is the tetrahedral-3 site, which the final site was four-fold and

the final position of the O atom was above the surface with a distance of 0.46 Å. This four-fold coordination was a distorted tetrahedral site with angles ranging from 80° to 125°, and differed from the PuGa-terminated bridge-PuGa-to-four-fold site. For the latter site, the four-fold coordination is in-plane to the PuGa surface and is a non-tetrahedral site (the angles significantly differ from a tetrahedral configuration). The interlayer separation of the tetrahedral-3 site, showed a contraction in d_{12} and d_{34} , while an expansion in d_{23} , but this expansion was significantly smaller, with a percent difference of 0.6%, then when no O adsorbate is present (percent difference of 3.7%). All interstitial sites showed an expansion of the bond lengths of the nearest neighboring atoms from the initial 2.26 Å and 1.96 Å for the octahedral and tetrahedral sites, respectively, which elucidates the stress/strain that the system experiences from the O atom being in the sub-surface. Also all final interstitial sites were a distorted interstitial site with percent error of the bond angles ranging between 0.01% to 9.95% and 1.06% to 26.60% for the octahedral and tetrahedral sites, respectively. Also the final tetrahedral-3 to four-fold adsorption geometry showed the O atom was protruding out of the surface, and was no longer a sub-surface site. Therefore we can conclude that on-surface O adsorption is preferred over interstitial adsorption.

4. Adsorption Probabilities

A simple Boltzmann distribution of the adsorption energies was computed to further quantify the on-surface versus sub-surface/interstitial adsorption probabilities on the Pu-terminated surface and interstitial sites. This was calculated using $P[E_i]/P[E_{i+1}] = e^{(E_i - E_{i+1})/k_B T}$ subject to the normalization condition that the sum of the Boltzmann probabilities is unity, where E_i denotes the adsorption energy at adsorption site i (i = top, bridge, hcp, fcc, etc.). Increasing i corresponds to increasing (unfavorable) chemisorption energies, and $T = 300$ K was assumed. The Boltzmann distribution illustrated that 93% of the time the oxygen atom will adsorb on the on-surface site, specifically the fcc site. Similarly for the PuGa-terminated surface, the

Boltzmann distribution showed a much larger on-surface adsorption probability of 99%. This suggests, assuming that the adsorption energies corresponds to at room temperature values, that oxygen diffusion must be activated, unless a significant amount of oxygen dosing is applied to the surface.

5. Adsorbate-induced work function changes

The results on the adsorbate-induced work-function changes with respect to the clean Pu-Ga surface, which is given by $\Delta\phi = \phi^{\text{adatom/PuGa}} - \phi^{\text{PuGa}}$, are shown in Table IV for the NSOC and SOC level of theory. The interstitials sites are not shown since the changes in work function were negligible (on the order of 0.01 eV). The least preferred sites have the largest change in work function (i.e. top site), while the most preferred sites have lowest change in work function (i.e. fcc site). These trends agree well with previous works.⁸⁻¹⁰ The work function shifts are explained as follows: partial transfer of electrons from the Pu-Ga surface to the O adsorbate occurs since O is more electronegative than both Pu and Ga; this results in an induced surface dipole formation; the magnitude of induced surface dipole moment is proportional to the change in work function.³² Another indicator was the change in magnetic moment. For instance, prior to adsorption the initial magnetic moment of the top site Pu was 3.97 μ_B . After O adsorption at the top site, the Pu magnetic moment decreased to 3.29 μ_B . Similar reduction was seen for other adsorption sites, such as the Pu-terminated bridge-to-fcc site where the average magnetic moment (averaged over the Pu atoms coordinated to oxygen) decreased from 3.96 μ_B before adsorption to 3.84 μ_B after adsorption. These reductions are signatures of charge transfer and substantiate the observed changes in the work functions, as reported in Table IV

B. Electronic structure

We commence the discussions on the electronic structure via partial density of states by focusing on the adsorption configurations for the least and most energetically favorable Pu-terminated sites, namely the bridge-to-fcc site. Figure 5 depicts the PDOS for the

aforementioned sites. Note that 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 (atoms are coordinated with O). In Figure 5, the degree of magnitude in the PDOS for the Pu *5f* states is much greater than the Pu *6d*, thus highlighting the interaction of the Pu *5f* states with the O *2p* states. The PDOS in Figure 5a shows hybridization and a broadening of the Pu *5f* and *6d* electrons with the O *2p* when compared to the bare relaxed Pu atoms. The O *2p* states are also at lower energies below the Fermi energy, which is in good agreement with Atta-Fynn's and Ray's work.^{9,10} For the bridge-to-fcc site (Figure 5b), the O *2p* states shift to an even lower energy state around 5 eV below the Fermi energy, while slight hybridization of Pu *5f* and *6d* with O *2p* is observed. The shift of the O *2p* states to lower energies for the favorable adsorption sites was also observed in Ref. 9 and 10. In general, both adsorption sites showed hybridization and a decrease in the *5f* and *6d* states in the vicinity of the Fermi level, thus indicating a net electron transfer from Pu to O. Note, that the hcp and fcc sites also showed this decrease in *5f* and *6d* electrons around the Fermi energy (not shown here). These features were similar to prior results reported in Ref. 9 and 10.

Next we will discuss the PDOS for the least and most energetically favorable for the PuGa-terminated surface, taking into account the cases where Ga forms or does not form a bond with O after adsorption (Figure 6). For the cases where Ga forms a bond with the O adatom, the Ga *4s* and *4p* states hybridize with the O *2p*, especially in the top-Ga site (Figure 6a). Furthermore, for the fcc-PuGa site (Figure 6b) the Pu *6d* intensity is comparable to the intensity for the *6d* states for the Pu-terminated PDOS results (Figure 5b). Also in Figure 6b, the degree of intensity of the *5f* states is similar to the Pu bare *5f* states and with a slight decrease in the *6d* states. Also no hybridization is observed between the Pu *5f* and O *2p* states, while very small hybridization of the Pu *6d* and O *2p* states is noted. The O *2p* states are located at lower energies in the fcc-PuGa adsorption site compared to the top-Ga adsorption site. A drop of the

Ga $4p$ states at the Fermi energy can also be seen for both sites. Thus, when Ga is participating in bonding to the O, the Ga atom affects the interaction between the Pu and O, by hindering the interaction of the Pu $5f$ states with the O $2p$ states.

In the case where Ga does not form a bond with O, the top-Pu site PDOS (Figure 6c) is similar to the Pu-terminated top site for the Pu $5f$ electrons, but the degree of hybridization of the Pu $6d$ at the Fermi energy is more evident than the Pu-terminated PDOS shown in Figure 5a. This feature may be further described if we only examine the Pu atoms before adsorption (Pu bare in Figure 5a and 6c). For the bare Pu atoms in Figure 5a, the PDOS shows a higher degree of intensity for the $5f$ and $6d$ states than the PuGa-terminated top-Pu site. This can be further explained by the fact that the Ga atom for this top-Pu site is a nearest neighboring atom (Pu-Ga bond length is 3.17 Å), and from the previous bulk Pu-Ga work,²³ the Ga $4p$ states hybridizes with Pu $6d$ states, while slightly decreasing the intensity of the $6d$ electrons. The prior Pu-Ga bulk studies also indicated that Pu $5f$ states remain unchanged. Therefore, even within the surface, the Ga atom enhances the ability of the $6d$ electrons to participate in bonding over the $5f$ electrons, which also aids in the stabilization of the surface (see earlier discussion). Subsequently, since the Pu $6d$ electrons are readily available, due to the Ga atom present on the surface, this allows for the O $2p$ states to hybridize strongly with the Pu $6d$ orbitals. Further indication of the affect of Ga to the Pu $6d$ states to hybridize with the O $2p$ states can be observed for the bridge-Pu-to-fcc site PDOS (Figure 6d).

For Figure 6d, the bridge-Pu-to-fcc site indicated that the degree of magnitude for $5f$ electronic states are similar to the Pu bare $5f$ electrons and hybridization and a further decrease (broadening) is observed in the Pu $6d$ states. These features can also be explained by the presence of the Ga atom at the surface. Also we observe a shift of the O $2p$ to lower energies for the more energetically favorable site, similarly to PDOS in Figure 5b, but there is splitting of the O $2p$ into sub-bands, which is not seen in the Pu-terminated PDOS (Figure 5b). This

splitting of the O $2p$, can be described by an indirect effect with the Ga atom present on the surface. Not shown in Figure 6c and 6d is that even though the Ga atom is not coordinated with the O adatom (after adsorption the O-Ga bond length is 5.22 Å for the bridge-Pu and 4.01 Å for the top-Pu site), the hybridization that is occurring between the Pu $6d$ and Ga $4p$ allows for this splitting to occur. This splitting of the O $2p$ is not observed in previous works done by Atta-Fynn and Ray^{9,10} with a pure Pu surface nor was it observed in the PDOS for the Pu-terminated surface (Figure 5). Therefore, the presence of Ga seems to decrease the propensity of the Pu $5f$ states to hybridize with the O $2p$ states. Therefore, allowing the Pu $6d$ to hybridize with the O $2p$ states, while also splitting the O $2p$ states into sub-bands. Hence, the presence of Ga at the surface greatly affects the electronic structure of the Pu atoms.

Next we will discuss the PDOS for the least and most energetically favorable interstitial adsorption sites for when Ga is either participating in bonding or not (Figure 7). Figure 7a and 7c, show that when a Ga-O bond is formed, the Pu $5f$ and O $2p$ hybridizations is negligible, while the Ga $4s4p$, Pu $6d$ and O $2p$ states is significant, with more pronounced splitting of the O $2p$ states. When the local environment is all Pu atoms (Figure 7b and 7d), we see a shift of the O $2p$ states to lower energies below the Fermi energy, coupled with very little hybridization between the Pu $5f$ and O $2p$ states, while there is some hybridization of the Pu $6d$, and no splitting of the O $2p$. Furthermore, Figure 7b and 7d show that the Pu $5f$ and $6d$ slightly become more broadened when compared to the PDOS for the bare Pu $5f$ and $6d$ states. The aforementioned findings further support the notion that O prefers an all Pu environment and that the splitting of the O $2p$ states is due to the presence of Ga, which was observed for the PuGa-terminated surface PDOS (Figure 6d). Even though the interstitial adsorption sites were not as energetically favorable compared to on-surface adsorption, the trends observed in the PDOS for the Pu-terminated and PuGa-terminated sites were consistent with the interstitial sites.

Finally a three-dimensional difference charge density plot is shown in Figure 8 for the Pu-terminated bridge-to-fcc site and for the PuGa-terminated bridge-PuGa-to-four-fold site. The difference charge density was computed as $\Delta n(r) = n(\text{Pu-Ga} + \text{O}) - n(\text{Pu-Ga}) - n(\text{O})$, where $n(\text{Pu-Ga} + \text{O})$ is the total charge density of the Pu-Ga system with adsorbate O, $n(\text{Pu-Ga})$ is the total charge density of the Pu-Ga slab, and $n(\text{O})$ is the charge density of the O atom. In the computations of $n(\text{Pu-Ga} + \text{O})$, $n(\text{Pu-Ga})$, and $n(\text{O})$, respective positions of the constituent atoms remained invariant. $\Delta n(r)$ provides a real space picture for assessing the redistribution of electron density due to the adsorption process. In Figure 8a, we notice electron density accumulation around the O atom (red regions) and electron density depletion around the Pu (blue regions). The electron density redistribution is further evidence by the data reported in Table V, which are the net valence partial charges (computed inside the muffin tin spheres) for the O adsorbate and the neighboring Pu atoms. For the Pu atoms, the net valence partial charges were calculated by taking the difference between the partial charges after O adsorption and the partial charges with no O present. For O, the difference is between the partial charge in the adsorbed state and the partial charges of the isolated atomic oxygen. A net reduction in the charge on all Pu atoms can be clearly seen in Table V, while a corresponding increase can be seen in the O atom. This is in agreement in the charge density redistribution plot in Figure 8a. Interesting enough, Figure 8b, where the O adatom is four-fold coordinated with three Pu atoms and one Ga atom, shows charge accumulation around the O atom while the Pu and Ga atoms are losing charge, while the net valence partial charges in Table V indicate that the charge transfer effects are still prevalent when Ga is involved in the bonding process, the net valence partial charge is less than the aforementioned site. Therefore, although the interaction is still there, the Ga atom seems to suppress Pu atoms to transfer significantly more charge to the O atoms.

IV. Conclusions

This work has reported atomic oxygen adsorption on a 3.125 at. % Ga stabilized δ -Pu (111) surface using all-electron density functional theory methods. We have discussed that Ga stabilizes the surface, due to the fact that formation energy and surface energy decreases with increasing Ga concentrations on the surface. Results indicated that the oxygen atom prefers an all Pu environment with three-fold coordination, with the highest chemisorption energy of -5.06 eV. Furthermore, we have discussed the impact of oxygen adsorption on the geometric stability of the surface. In addition, the partial density of states indicated a delocalization of the $5f$ and $6d$ states and hybridization of Pu $5f$ and $6d$ states with the O $2p$ states at the Fermi energy for when the oxygen interacts with an all Pu environment, thus implying the high reactivity of Pu with O. When the adsorption configuration includes a Ga-O bond, chemisorption energies are less favorable compared to the configuration with only Pu-O bonds. Furthermore, the Ga atom inhibits the ability for the Pu atoms' $5f$ to hybridize with the O $2p$ orbitals, while enhancing the ability of the $6d$ orbitals to hybridize with O $2p$ orbitals. Finally, the O atom prefers to adsorb on the surface, since the interstitials sites were not as favorable as the surface sites. Finally, the aforementioned results indicate that Ga discourages the formation of an oxide layer on δ -Pu.

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Table I: Results for the Pu-terminated surface which includes relaxation energy, E_r , chemisorption energy, E_c , at the NSOC and SOC level of theory, and distance of the adatom from the surface, r_{slab-O} , and distance of the adatom to the nearest neighboring atoms, r_{Pu-O} .

Pu-terminated			NSOC	SOC		
Initial site	Final site	E_r (eV)	E_c (eV)	E_c (eV)	r_{slab-O} (Å)	r_{Pu-O} (Å)
top	top	-0.27	-3.46	-3.55	1.86	1.86
hcp	hcp	-0.27	-4.50	-4.65	1.31	2.26, 2.26, 2.36
fcc	fcc	-0.55	-4.80	-4.91	1.07	2.23, 2.24, 2.27
bridge	fcc	-0.97	-4.90	-4.98	1.11	2.20, 2.24, 2.30

Table II: Results for the PuGa-terminated surface which includes relaxation energy, E_r , chemisorption energy, E_c , at the NSOC and SOC level of theory, and distance of the 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 adatom. Note if atom is not designated by parenthesis it is assumed that it is a Pu atom.

PuGa-terminated			NSOC	SOC		
Initial site	Final site	E_r (eV)	E_c (eV)	E_c (eV)	r_{slab-O} (Å)	r_{X-O} (Å)
top-Pu	top	-0.24	-3.36	-3.50	1.86	1.86
top-Ga	top	-0.43	-1.69	-1.62	1.80	1.80 (Ga)
hcp-Pu	hcp	-0.55	-4.82	-4.83	1.02	2.23, 2.23, 2.29
hcp-PuGa	hcp	-0.27	-3.76	-3.85	1.17	2.16, 2.16, 2.22 (Ga)
fcc-Pu	fcc	-0.51	-4.83	-4.94	1.11	2.23, 2.23, 2.34
fcc-PuGa	fcc	-0.33	-4.01	-4.09	1.16	2.18, 2.21 (Ga), 2.25
bridge-Pu	fcc	-1.05	-4.95	-5.06	1.07	2.24, 2.26, 2.28
bridge-PuGa	four-fold	-0.69	-3.92	-4.01	0.89	2.16 (Ga), 2.21, 2.31, 2.93

Table III: Results for the interstitials sites which includes relaxation energy, E_r , chemisorption energy, E_c , at the NSOC and SOC level of theory, and distance of the 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 adatom. Note if atom is not designated by parenthesis it is assumed that it is a Pu atom.

Interstitials		E_r (eV)	NSOC E_c (eV)	SOC E_c (eV)	r_{slab-O} (Å)	r_{X-O} (Å)
Initial site	Final site					
octahedral-1	octahedral*	-0.39	-4.09	-4.02	-1.28	2.31, 2.34, 2x2.38, 2.42, 2.55 (Ga)
octahedral-2	octahedral*	-0.43	-4.45	-4.40	-3.95	2x2.39, 2x2.40, 2.41, 2.42
octahedral-3	octahedral*	-0.38	-4.65	-4.55	-1.15	2x2.37, 2.39, 2.41, 2.42, 2.43
tetrahedral-1	four-fold	-0.77	-4.00	-4.02	-0.05	2.12 (Ga), 2x2.21, 2.46
tetrahedral-2	tetrahedral*	-0.41	-4.10	-4.03	-3.26	3x2.25, 2.27
tetrahedral-3	four-fold	-0.38	-4.66	-4.64	0.46	2x2.22, 2.28, 2.77

*Final site was a distorted interstitial site, unless otherwise noted.

Table IV: Changes in work function, $\Delta\phi$, at the NSOC and SOC levels of theory. The work function for the clean relaxed Pu slab was 3.29 eV and 3.37 eV, respectively, at the NSOC and SOC level of theory. Experimental work function is 3.2 eV.³¹

		NSOC $\Delta\phi$ (eV)	SOC $\Delta\phi$ (eV)
Initial site			
Pu-terminated	top	0.28	0.28
	hcp	0.16	0.15
	fcc	0.10	0.09
	bridge	0.12	0.11
PuGa-terminated	top-Pu	0.33	0.33
	top-Ga	0.22	0.22
	hcp-Pu	0.09	0.08
	hcp-PuGa	0.11	0.10
	fcc-Pu	0.10	0.09
	fcc-PuGa	0.12	0.12
	bridge-Pu	0.11	0.11
	bridge-PuGa	0.07	0.06

Table V: Net valance partial charges for the Pu-terminated bridge-to-fcc site and PuGa-terminated bridge-PuGa-to-four-fold site.

Surface	Initial site	Atom	Net Valance charge
Pu-terminated	bridge	Pu	-0.049
		Pu	-0.029
		Pu	-0.019
		O	0.266
PuGa-terminated	bridge-PuGa	Pu	-0.045
		Pu	-0.062
		Pu	-0.038
		Ga	0.008
		O	0.186

Figure 1: 3.125 at. % Ga stabilized δ -Pu surface, with Ga located in the topmost surface. Pu atoms are yellow, while Ga atoms are purple. Visualization from Ref. 27.

Figure 2: Initial sites for oxygen (blue) adsorbate. 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. Sites include positions where the oxygen atom regresses further away from the Ga atom [(a)-(c)].

Figure 4: Top (a) and side (b) view of the final geometries for the Pu-terminated bridge-to-fcc site.

Figure 5: Partial density of states for the SOC level of theory for the least favorable site, top site (a), and most favorable site, bridge-to-fcc site (b), for when the O adsorbate 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 and top-Pu site [(a) and (c), respectively], and most favorable site, fcc-PuGa and bridge-Pu site [(b) and (d), respectively], for when the O absorbate is approaching the PuGa-terminated surface.

Figure 7: Partial density of states for the SOC level of theory for the least favorable interstitial site, tetrahedral-1 and octahedral-1 [(a) and (c), respectively], and most favorable site, tetrahedral-3 and octahedral-3 site [(b) and (d), respectively], for when the O absorbate is initially placed in an interstitial site.

(a)

(b)

Figure 8: Three-dimensional charge density difference, $\Delta n(r)$, for the bridge-to-fcc site (a) for the Pu-terminated surface, and for the PuGa-terminated surface, the bridge-PuGa-to-four-fold 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.