Ab Initio Study of the Effect of Mono-Vacancies on the Metastability of Ga-Stabilized δ-Pu

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Abstract: Most experimental studies on metallic Pu are on the room temperature monoclinic α-phase or the fcc Ga stabilized δ-phase. Stabilized δ-phase Pu-Ga alloys are metastable and exhibit a martensitic phase transformation to α′-phase at low temperatures, or applied shear, with concentrations lower than three atomic percent Ga. By using first principles, we explore the metastability of δ-phase by investigating the structural and electronic behavior induced by Ga alloying and by a mono-vacancy point defect. We find that a site substitutional Ga induces a tetragonal distortion in the lattice affected by hybridization of Ga 4p and Pu 6d states. With the addition of a mono-vacancy, a monoclinic or tetragonal distortion forms locally (dependent on its distance from Ga), and decoupling of the Pu 5f and 6d states and broadening of the 6d states occurs. This response enables hybridization of Pu 6d with the Ga 4p states affecting the mono-vacancy formation energy. Thus, stabilization of the fcc lattice correlates with hybridization of Pu 6d states with Ga 4p states, and this becomes more evident in the presence of a mono-vacancy.

Keywords: plutonium; point defects; metastability; gallium; electronic structure

1. Introduction

Plutonium (Pu) metal is considered one of the most complex metals in the periodic table due to 5f electronic behavior of being delocalized or localized depending on the atomic environment. Elemental plutonium undergoes five solid-state phase transformations starting with its complicated room temperature 16-atom simple monoclinic α-phase, to the 34-atom body-centered-monoclinic β-phase, and then the eight-atom face-centered orthorhombic γ-phase to the highest temperature highly symmetric face-centered-cubic (fcc) δ-phase [1]. Beyond this phase is the body-centered-tetragonal δ′-phase and the body-centered-cubic ε-phase, right before the low melting temperature of 913 K [2], and the δ and δ′ phases undergo a negative thermal expansion. This complicated phase diagram is attributed to the variable nature of the Pu 5f electrons and its atomic environments.

Since the α-phase is brittle, like cast iron, the ductile δ-phase is most often used for technological applications. For ductile δ-phase production, Pu is stabilized usually with a Group IIIA element such as aluminum, gallium (Ga), and indium. The stabilization of the δ-phase to room temperature is dependent on alloying solute concentration, with as little as one atomic percent (at. %) Ga may stabilize the fcc phase [3], but upon cooling or mechanical shear, this alloy will undergo a martensitic phase transformation to an expanded α-phase lattice (identified as α′-phase) retained to ambient conditions. These stimuli are no longer effective at producing retained martensitic phase beyond ~3 at. % Ga and the δ-phase negative thermal expansion changes to a positive thermal expansion [4–8].
The metastability of Ga-stabilized $\delta$-Pu at room temperature is dependent on the solute alloy concentration but is also dependent on defects and their influence on the local atomic environment and electronic structure. On this subject, many fundamental questions remain unanswered. One source of defect production in Pu is self-irradiation, which occurs via alpha emission by a decay into daughter products of uranium and helium nuclei causing lattice damage in the form of Frenkel pairs (interstitial and mono-vacancy) [9,10]. Interest in the self-irradiation of Pu has led to insightful work showing unconventional defect-induced fcc stabilization of $\delta$-Pu-Ga alloys against martensitic phase transformation [11], providing theoretical analysis into the influence of daughter product ingrowth and why there has been no detected void swelling in fcc Ga stabilized $\delta$-Pu [12]. There are conflicting studies of the Ga influence on the lattice swelling observed under self-irradiation, and it remains unclear if increasing Ga concentrations either increase or have no influence on the relative lattice swelling [13,14]. However, recent extended x-ray absorption fine structure (EXAFS) studies show that during isochronal annealing, the cryogenically accumulated local defect environment is different around the Pu than around the Ga [15]. Understanding defect to damage evolution is extremely important to our understanding of Ga-stabilized $\delta$-Pu alloy phase metastability. This is most evident for the two Pu-Ga phase diagrams—one founded in metastability (US) and the other in thermodynamic equilibrium (Russian)—in which the kinetically favorable means of progression from one to the other is by damage-induced eutectoid decomposition of $\delta$-Pu to $\alpha+Pu_3Ga$ in less than $10^4$ h [16,17]. Otherwise, computational coupling of phase diagrams and thermochemistry (CALPHAD) calculations have concluded that the kinetics for decomposition will not occur until after $1.5 \times 10^6$ years [18].

By using density functional theory (DFT), we can systematically investigate the metastability of Ga-stabilized $\delta$-Pu at a fundamental level by exploring various defects and the role of the alloying solute Ga. In this paper, we baseline Ga alloying behavior as a $\delta$-phase stabilizer, then focus on the mono-vacancy at various distances from the Ga atom and in different Ga concentrations. We calculate that the local lattice distortions are characteristics of the low-symmetry Pu phases, such as the monoclinic phase, and recognize in the local lattice and electronic structures that there is a delicate balance between the Ga 4p and Pu 5f and 6d states, as competing interactions are revealed through local distortion and formation energies of the mono-vacancy defect.

2. Materials and Methods

All calculations implemented the Vienna Ab initio Simulation Package [19–22] and the Perdew-Burke-Ernzerhof formulation to the generalized-gradient approximation for the exchange-correlation functional [23,24]. By using a $3 \times 3 \times 3$ fcc lattice supercell (108 inequivalent atoms), we may gauge the short- and long-range effects of the stabilization solute, Ga, and the mono-vacancy defect. In addition, this supercell has numerous nearest neighboring (nn) shells complete, i.e., the first (1nn), second (2nn), third (3nn), fourth (4nn), and sixth (6nn) are filled. The seventh (7nn), ninth (9nn), and 10th (10nn) are incomplete, and there is no atoms in the eighth (8nn) shell due to the finite size of the supercell and periodic boundary conditions. The Ga concentrations investigated included 0.926, 1.852, and 2.778 at. % Ga, and in cases where there are multiple Ga atoms, the Ga atoms where located at 4nn distance in a substitutional Pu site from each other since this was determined to be the most energetically favorable site and as observed in EXAFS data (Figure 1) [3,25–28].

Density functional theory has determined that for metallic Pu an anti-ferromagnetic (AFM) arrangement is the ground state [29,30], even though it has been experimentally determined that there is no static long range ordering [31]. By using an AFM configuration, this allows for a continuous description of the electronic structure throughout the many phases of Pu [29]. The use of magnetism within DFT allows an approximation for the strongly correlated 5f electrons and provides comparable structural properties to experimental data [25,30], which allows a first-principles approach to understanding the complex energetic potential landscape for defects as these calculations require the use of supercells. We would also like to note that a non-magnetic configuration significantly contracts the lattice [25], and test calculations with the Ga atom yielded an instability of site substitutional Ga,
unless the volume is contracted. As for theoretical methods beyond DFT, such as dynamical mean field theory, there is an inherent limitation of the theory that will not allow the use of supercells that are necessary for representation of the symmetry breaking due to a defect or alloying solute [32,33]. Theoretical work extending to the Hubbard U model (DFT+U) has recently suggested that a small U value of \( \sim 1 \) eV may be used for Pu [34] instead of the higher value of \( \sim 4 \) eV [35], and it has also been shown that \( \delta \)-Pu is highly sensitive to the U value in lattice parameter, bulk modulus, and density of states [36]. Söderlind et al. [30] also calculated that the larger U value (~4 eV) will give the unalloyed \( \delta \)-phase an unphysical lower energy than the \( \alpha \)-phase. Thus, in general, Pu is highly sensitive to the chosen value of U, and since it is expected that local distortions may take on the form as the low symmetry phases of Pu [37,38], which exhibit a higher degree of delocalization than the \( \delta \)-phase [30,33], the addition of a U value could highly restrict this natural progression of possible theoretical mechanisms of destabilization.

Additional theoretical works have taken into account a disordered moment as a stabilization mechanism for \( \delta \)-Pu and have explored this along with other stabilization alloying impurities in addition to Ga [39–42]. For the purpose of this work, the Pu atoms were configured as a spin-polarized AFM arrangement with no spin-orbit coupling and orbital polarization added. It has been determined that the addition of relativistic effects (spin-orbit coupling and orbital polarization) compensates for the spin-polarization effects [43]. In addition, energetic trends predicted by DFT will not significantly change as it has been calculated that the energy difference between no-spin-orbit-coupling and spin-orbit-coupling for formation energies of a vacancy in 3.125 at. % Ga \( \delta \)-Pu was on average \( \sim 0.1 \) eV [25]. It also has been shown that using spin-orbit-coupling and orbital polarization with a non-magnetic configuration for \( \delta \)-Pu yields reasonable equilibrium volume and bulk modulus compared to experimental values [43], but regardless, the AFM configuration is still lower in energy when the relativistic corrections are added implying the importance of spin within the complex electronic correlation of Pu [44]. Furthermore, it has been observed experimentally that defects induced localized magnetic moments in both Ga-stabilized \( \delta \)-Pu and \( \alpha \)-Pu [45], and thus, we believe using an AFM spin-polarized as a first-principles approximation for the strongly correlated 5f electrons is justified for Pu.

The equilibrium theoretical lattice constant was calculated via volume optimization (preserving cubic symmetry), and then, these structures underwent an ionic relaxation (including ions located at the periodic boundary) with Ga substitutional impurities and then an additional ionic relaxation was performed when the mono-vacancy was included. This process mimics a dilute case of an impurity and/or defect in an “infinite” bulk system [46]. Computational parameters include a kinetic energy plane-wave cutoff of 500 eV, Γ-point k-point mesh using the Monkhorst–Pack scheme, energy convergence of \( 1 \times 10^{-5} \) eV, and ions are relaxed until the Hellmann–Feynman forces on each ion is less than 0.01 eV/Å.

![Figure 1. Ga-stabilized δ-Pu structures with (a) 0.926, (b) 1.852, and (c) 2.779 at. % Ga concentrations. The yellow atoms are Pu and purple atoms are Ga. In structures that have multiple Ga atoms, the Ga is placed at fourth nearest neighboring distances from each other.](image-url)
Two equations were used to calculate formation energies, one for the energy required to form the Pu-Ga alloys and another for the addition of the mono-vacancy within the lattice. The formation energy ($E_{\text{f}}^{\delta\text{Pu-Ga}}$) of the Pu-Ga alloys is

$$E_{\text{f}}^{\delta\text{Pu-Ga}} = E_{\delta\text{Pu-Ga}} - \frac{x}{108} E_{\delta-\text{Pu}} - \frac{y}{8} E_{\alpha-\text{Ga}},$$  

(1)

where $E_{\delta\text{Pu-Ga}}$ is the total energy of the lattice with Ga, $x$ is the number of Pu atoms in the Pu-Ga lattice, $E_{\delta-\text{Pu}}$ is the total energy of the pure $\delta$-Pu lattice, $y$ is the number of Ga atoms in the Pu-Ga lattice, and $E_{\alpha-\text{Ga}}$ is the total energy of the orthorhombic 8-atom $\alpha$-Ga bulk crystal. Reference states for the Ga were fully optimized and treated with no spin-polarization. Formation energy ($E_{\text{f}}^{\text{vac}}$) for a mono-vacancy is

$$E_{\text{f}}^{\text{vac}} = E_{\text{defect}} - E_{\delta\text{Pu-Ga}} - \frac{x}{108} E_{\delta-\text{Pu}},$$  

(2)

where $E_{\text{defect}}$ is the total energy of the Pu-Ga lattice with defect, $E_{\delta\text{Pu-Ga}}$ is the total energy of the lattice with Ga, $x$ is the number of Pu atoms in the defective Pu-Ga lattice, and $E_{\delta-\text{Pu}}$ is the total energy of the pure $\delta$-Pu lattice with no defects.

3. Results

3.1. Structural Effects

Before we discuss the structural effects due to a defect, we would like to first note the structural effects due to Ga alloying. Table 1 shows a summary of the equilibrium lattice constants and formation energies for the $\delta$-Pu-Ga structures investigated in this study. The formation energies are exothermic and the equilibrium lattice constant decreases with increasing Ga concentrations, which agrees with experimental results, but with a consistent contraction of ~2.6% difference (Figure 2) [3,47]. Formation energies also follow a similar trend as calculated with previous DFT studies [25,26,48]. In a pure $\delta$-Pu fcc lattice with no Ga, there are no structural effects locally, but the presence of a substitutional Ga induces a tetragonal distortion along the spin axis (100) plane. This is evident in the 1nn radial distribution functions (RDF) shown in Figure 3. For the 0.926 at. % Ga structure four Pu atoms decrease inward by 0.13 Å and the remaining eight Pu atoms decrease inward by 0.06 Å. This tetragonal distortion due to the Ga transmits through the 2nn shell but is minimal with only a 0.04 Å decrease. As the Ga concentration increases, this tetragonal distortion becomes more evident due to the competing interactions of the Ga within the cell and the increase of short-range disorder [25,48]. This varying distances from the Ga was observed via EXAFS in Pu-Ga alloys, which was also dependent on the proximity to the Ga atoms [27,49]. EXAFS data has found overlapping Ga-centered 3nn shells influences the local environment around all Pu atoms [27], and this effect increases at higher Ga concentrations [49]. The magnitude of the Pu-Ga bond length contractions within the supercell are in reasonable agreement with EXAFS observations.

Table 1. Equilibrium lattice constants and formation energies ($E_{\text{f}}^{\delta\text{Pu-Ga}}$) in eV/atom and kJ/mol for 0.926, 1.852, and 2.778 at. % Ga $\delta$-Pu structures.

| % at. Ga | $a_0$ (Å) | $E_{\text{f}}^{\delta\text{Pu-Ga}}$ (eV/atom) | $E_{\text{f}}^{\delta\text{Pu-Ga}}$ (kJ/mol) |
|----------|----------------|--------------------------------|----------------------------------|
| 0        | 4.524          | -                             | -                                |
| 0.926    | 4.520          | -0.010                        | -0.944                           |
| 1.852    | 4.515          | -0.019                        | -1.807                           |
| 2.778    | 4.501          | -0.030                        | -2.867                           |
Figure 2. Experimental and density functional theory (DFT) calculated lattice parameters as a function of Ga dependency. Experimental data is from Ellinger et al. [3].

Figure 3. Radial distribution functions (RDF) for 0 (pure), 0.926, 1.852, and 2.778 at. % Ga δ-Pu structures from the perspective of the Ga atom when applicable. Nearest neighboring shells include first, second, third, fourth, fifth, sixth, seventh, ninth, and tenth.

The effects of Ga on the local distortion induced by the mono-vacancy is evident. In the 0.926 at. % Ga structure, depending on the distance from the Ga, the distortion either is tetragonal or monoclinic, similar to what was calculated in the pure δ-Pu [38]. The formation energy increases as compared to a mono-vacancy in pure δ-Pu (1.23 eV for tetragonal distortion and 1.08 eV for monoclinic distortion [38]) when the mono-vacancy is 1nn to the Ga. Other DFT calculations that used an AFM or disordered local moment configuration for a mono-vacancy in δ-Pu calculated 1.34 eV and 1.07 eV [42], respectively, which are similar to our previously calculated values [38]. Surprisingly, a mono-vacancy at 1nn to the Ga formed a monoclinic local distortion in the <100> direction away from the Ga atom with formation energy of 1.39 eV (Figure 4a). The Ga atom shares four nearest neighboring bonds that comprise atoms within the one mirror symmetry plane for the monoclinic distortion due to the vacancy and from the
RDF there are some atoms from the 1nn and 2nn shell that have relaxed from the lattice site due to this distortion (Figure 5). When the mono-vacancy is located at 2nn from the Ga atom, the formation energy increases to 1.48 eV, and then farther away at 6nn, the formation energy decreases to 1.25 eV, which is similar in energy to the tetragonal distortion calculated in the pure system with no Ga. The distortion is similar to the tetragonal distortion as shown in the RDF plot in Figure 5.

**Figure 4.** Distortion induced by a mono-vacancy at first nearest neighbor to a Ga atom for (a) 0.926, (b) 1.852, and (c) 2.778 at. % Ga, and (d) when the mono-vacancy is located at fourth nearest neighboring distance from the Ga for the 2.778 at. % Ga. For (a) and (b) only the distortion is shown, and the entire structure is shown for (c) and (d). Yellow and purple atoms are the Pu and Ga atoms, respectively, and Pu-Pu bonds >3.0 Å are shown in black.

**Figure 5.** Radial distribution function (RDF) of a mono-vacancy from first (1nn), second (2nn), and sixth (6nn) nearest neighboring distance from the Ga atom for 0.926 at. % Ga. RDF is calculated from the perspective of the Ga atom.
For the 1.852 at. % Ga structures with a mono-vacancy, there are two Ga atoms in the cell, and we begin to observe competing effects. When the mono-vacancy is 1nn distance from only one Ga atom, the formation energy increases to 1.49 eV as compared to the 0.926 at. %, and the monoclinic distortion is still present, even though the second Ga atom is at 3nn distance away from the vacancy [Figure 4b]. The RDF is similar to the 0.926 at. % Ga case when the vacancy is 1nn to the Ga (Figure 6). The formation energy remains the same at 2nn distance (1.50 eV) and then decreases to a similar formation energy as observed in the pure and 0.926 at. % Ga results to 1.22 eV when the vacancy is located at 7nn distance from the Ga. When the mono-vacancy is interacting with both Ga atoms at either 1nn or 2nn, the formation energy increases even more to 1.58 eV and 1.61 eV, respectively. It is evident from the RDF plot (Figure 5) that even though the formation energy is the highest among mono-vacancy structures that were investigated in this work, the stability of the fcc crystal is the highest (Figure 6), i.e., least distorted fcc lattice. The mono-vacancy at 1nn shows the local instability of the fcc lattice in the RDF (Figure 6), while when located at 7nn, we observe a similar tetragonal distortion as the 0.926 at. % Ga case.

![Radial distribution function (RDF) of a mono-vacancy from first (1nn), first in between two Ga atoms (1nn bw 2Ga), second in between two Ga atoms (2nn bw 2Ga), and seventh (7nn) nearest neighboring distance from the Ga atom for 1.852 at. % Ga. RDF is calculated from the perspective of the Ga atom.](image)

**Figure 6.** Radial distribution function (RDF) of a mono-vacancy from first (1nn), first in between two Ga atoms (1nn bw 2Ga), second in between two Ga atoms (2nn bw 2Ga), and seventh (7nn) nearest neighboring distance from the Ga atom for 1.852 at. % Ga. RDF is calculated from the perspective of the Ga atom.

With an increase in Ga to 2.778 at. %, the trend remains the same as the 1.852 at. % Ga results, such as the formation energy increases at 2nn distance (1.44 eV) and then decreases when the mono-vacancy is the farthest away at 7nn distance (1.17 eV). The local monoclinic distortion that was observed when the mono-vacancy was 1nn to the Ga in the 0.926 and 1.852 at. % Ga structures is no longer present for the 2.778 at. % Ga concentration [Figure 4c], but is a tetragonal distortion in nature (Figure 7). The highest stability least distorted fcc lattice from the RDF in Figure 7 occurs when the mono-vacancy is 2nn between three Ga atoms, but with a significant increase of formation energy of 1.75 eV. As the mono-vacancy is further away from the Ga, the monoclinic distortion reappears at 4nn distance away from the Ga as shown in Figure 4d with a significant drop in formation energy to 1.10 eV. This is very close in energy to the monoclinic distortion induced by a mono-vacancy calculated in pure δ-Pu with formation energy of 1.08 eV [38]. The RDF also indicates this instability of the structure as
the atoms are slightly off their lattice positions around the 7nn and 9nn shell distance from the Ga (Figure 7). A summary of formation energies of the various mono-vacancies studied in this work are shown in Table 2.

Table 2. Formation energies ($E_{\text{vac}}^f$) of mono-vacancy at varying distances from the Ga.

| at. % Ga | Distance from Ga | $E_{\text{vac}}^f$ (eV) |
|---------|-----------------|-----------------|
| 0.926   | 1nn             | 1.39            |
|         | 2nn             | 1.48            |
|         | 6nn             | 1.25            |
| 1.852   | 1nn             | 1.49            |
|         | 1nn between 2 Ga| 1.58            |
|         | 2nn             | 1.50            |
|         | 2nn between 2 Ga| 1.61            |
|         | 3nn             | 1.22            |
| 2.778   | 1nn             | 1.39            |
|         | 1nn between 2 Ga| 1.57            |
|         | 2nn             | 1.44            |
|         | 2nn between 2 Ga| 1.53            |
|         | 2nn between 3 Ga| 1.75            |
|         | 4nn             | 1.10            |
|         | 7nn             | 1.17            |

The above results suggest that the monoclinic distortion is induced in all Ga concentrations, and the formation energy and orientation of this distortion is dependent on the distance the mono-vacancy is from the Ga atoms. We would like to note that a variation of this distortion does form (not shown) when the mono-vacancy was far from the Ga in the 0.926 and 1.852 at. % Ga concentrations, but the change in formation energy was not as significant, as calculated in the 2.778 at. % Ga concentration. Another general trend is the increase of the formation energy when the mono-vacancy is located at 2nn
distance from the Ga atom when compared at 1nn distance. This implies that the Ga interaction is still influential up to the 2nn shell suggestive of superexchange interactions. This trend is also present in a previous all-electron DFT study of hydrogen-vacancy complexes in 3.125 at. % Ga, where the calculated formation energies of a vacancy from the Ga increased from 0.76 eV for 1nn to 1.05 eV for 2nn distance and then decreased to 0.76 eV at 4nn distance from the Ga [25], and this trend did not change with the inclusion of spin-orbit coupling.

3.2. Electronic Structure

The partial density of states (PDOS) are shown for select Pu atoms within the structure with varying distances from the Ga atom (Table 3) for the Pu-Ga structures with no defects and defects. First, we will discuss the PDOS with no defects shown in Figure 8, where Pu-1 and Pu-2 are atoms that are 1nn distance from the Ga and Pu-3 is from a nearest neighbor shell further away in order to gauge the effects on Pu near or far from the Ga. Clearly, in Figure 8, the Ga 4p states are located in the same energy region and the Pu 5f states exhibit similar features for all three concentrations. The PDOS for Pu-1 has an increased 5f intensity at ~0.4 eV as compared to Pu-2 and Pu-3. Due to the induced tetragonal distortion from the Ga, Pu-1 is slightly closer to the Ga atom than Pu-2, and this enables Ga 4p and Pu 6d hybridization at approximately 2.25 eV below the Fermi energy. Not shown is the fact that the Pu 6d orbital states allow for hybridization with the Ga 4p states where the Pu 5f orbital states are heavily weighted at the Fermi energy. Another note is that the Ga 4p_y and 4p_z states are equivalent in the 0.926 at. % Ga concentration apparently due to the tetragonal distortion that occurs in the y-z plane. Increasing the Ga content in the structure, the Ga 4p_y and 4p_z states shift from one another but have similar structure, and the Pu 6d states decrease in intensity with an emergence of higher intensity 6d state in the Pu-3 atom at an energy of around −2 eV, indicating competing interactions of the Ga atoms within the structure. It has been previously calculated that when spin-orbit coupling is taken into account, the Pu–Ga interactions are still dominated by Pu 6d and Ga 4p hybridization [25].

| at. % Ga | Defect Distance to Ga | Pu-Ga Distance (Å) | Pu-vacancy Distance (Å) |
|---------|-----------------------|--------------------|------------------------|
| 0.926   | No Defect             | 3.07               | 3.14                   |
| 1.852   | No Defect             | 3.08               | 3.18, 3.18             |
| 2.778   | No Defect             | 3.06               | 3.16, 3.15             |
| 0.926   | 1nn                   | 3.07               | 3.88                   |
| 1.852   | 1nn                   | 3.06               | 3.10, 3.17             |
| 2.778   | 1nn                   | 3.10               | 5.40                   |
| 2.788   | 1nn bw 2Ga            | 3.03               | 3.12, 3.19             |
| 2.788   | 2nn bw 3Ga            | 3.13               | 5.49                   |
| 2.788   | 4nn                   | 3.02               | 5.53                   |

The importance of spin as part of the electronic correlation is highlighted further in the Supplementary Materials. In Figure S1, when the PDOS is calculated for a pure δ-Pu (at the AFM theoretical lattice constant) for a non-magnetic configuration, the Pu 5f electrons intensity significantly increases right below the Fermi energy in contrast with the AFM configuration. This causes the Pu 6d states to shift to higher energies. Hence, this changes the bonding mechanism when Ga is introduced into the lattice where the Ga 4p states hybridizes with the Pu 5f states when considering a non-magnetic configuration in the AFM structure (Figure S2).
With the introduction of a mono-vacancy at the first nearest neighboring distance from the Ga, there is minimal change in the Ga 4p states, while there are distinct changes in the Pu 5f and 6d states (Figure 9). For instance, in the 0.926 at. % Ga structure where a monoclinic distortion formed, the 5f states for Pu-2 shifts right below the Fermi energy and a broadening of the Pu 6d states, which was also observed in the pure δ-Pu when a monoclinic distortion formed [38], indicating a monoclinic structural distortion and the associated electronic structure response [33]. With the increase of Ga concentration to 1.852 at. % Ga, a similar monoclinic distortion appeared and there are no longer 5f states right below the Fermi energy as they have shifted to lower energies. There is still an observed broadening of the Pu-1 and Pu-2 5f and 6d states. At the 2.778 at. % Ga concentration, the Pu 5f states shifts even further below the Fermi energy with a decrease in the Pu 6d states for the atom closest to the Ga atom (Pu-1). Hence, the PDOS in Figure 9 suggests the stabilization of the fcc matrix by decreasing the Pu 6d states below the Fermi energy with a decrease in the Pu 6d states for the atom closest to the Ga atom (Pu-1). 

We will now discuss the effects when the mono-vacancy is interacting with multiple Ga atoms in the 2.778 at. % Ga concentration. In the case where the mono-vacancy is located in between two Ga atoms at the first nearest neighboring distance, the PDOS shows an increase of the 5f states shifted right below the Fermi energy to promote Pu 6d and Ga 4p hybridization in this region for the Pu-1 and Pu-2 atoms (Figure 10). However, as indicated above, the fcc structure is locally preserved, but there is an energetic cost, as the formation energy increases to 1.57 eV. This is further highlighted when the mono-vacancy is in between three Ga atoms at the second nearest neighbor distance, there is no change to the Pu 5f states regardless of the distance from the Ga atom, and the Pu 6d states are similar to when there is no defect. The energetic cost is even higher in order to maintain the undistorted fcc lattice structure since the formation energy increased to 1.75 eV, thus implying that the fcc stability is most likely due to Ga-Ga repulsion [25]. Once the mono-vacancy is further out from the Ga, such as 4nn distance, formation energy decreases to 1.10 eV, a monoclinic distortion forms, and the PDOS takes on the form as observed in pure δ-Pu [38] and 0.926 at. % Ga case discussed above (Figure 9).
4. Discussion

The above results highlight the structural and electronic stability of the fcc lattice due to competing effects of the stabilizing solute Ga atom and a mono-vacancy. While there are some structural distortions due to the mono-vacancy, such as a monoclinic or tetragonal distortion, the electronic effects indicate
a complex balance between the Pu 5f and 6d states. Due to the strong coupling of the Pu 5f and 6d states [50–53], in order for the Ga to stabilize the fcc matrix, hybridization of the Ga 4p and Pu 6d states must occur. With the introduction of a mono-vacancy, 5f–6d states decouple, thus intensifying the 5f states near the Fermi energy and broadening the 6d states, enabling hybridization with the Ga 4p states. This mechanism provides the lowest formation energy by exchanging between fcc lattice structural stability against electronic structure changes, as formation energy increases due to Ga-Ga repulsion. The Ga atoms energetically prefer to be non-interacting and only interacting with Pu atoms [25,54]. The absence of a lattice Pu atom between Ga atoms induces an interaction between the Ga atoms that is repulsive thus prompting strain on the lattice in the opposite direction from the local induced vacancy distortion in order to maintain the fcc lattice. These local structural changes are energetically costly raising the defect formation energy. This model behavior is amazingly similar to that observed in EXAFS experiments of local structure in Ga stabilized fcc δ-phase alloys by Conradson, et al. [55], i.e., the local environment of the calculated defect structures bear remarkable similarity to the traits of the proposed “σ-phase.” This proposed phase are nanoscale regions absent of Ga and intimately associated with the host matrix, but the size and coherence are at or below the diffraction limit. The presence of the Ga atom will affect the local distortions induced by defects but will also affect their formation energies. It is expected that Ga will also affect migration of these defects, as reviewed in experimental results [56] and recently calculated for mono-vacancy and split-interstitial defects in pure δ-Pu [57].

5. Conclusions

In conclusions, by exploring the structural and electronic effects within the Ga stabilized fcc δ-phase alloy and introducing a mono-vacancy in the lattice using DFT, we are able to obtain insights into its fcc lattice stabilization mechanism. Due to the chosen spin-structure in the lattice, the Ga structurally induces a tetragonal distortion, while intensifying the Pu 5f states of atoms located in the tetragonal plane due to the decoupling of the Pu 5f-6d states to enable Pu 6d hybridization with the Ga 4p states. The inclusion of a mono-vacancy within the lattice near or far from the Ga introduces a monoclinic or tetragonal distortion locally, which depending on the Ga concentration, will promote Pu 5f electrons to the Fermi energy while broadening the Pu 6d states to again enhance hybridization with the Ga 4p states. As for when the mono-vacancy is interacting with multiple Ga atoms within the lattice, the stability of the lattice increases, as there are no significant local distortions. However, in order to maintain fcc stability, hybridization of the Ga 4p and Pu 6d states must occur, thus leading to an increase in defect formation energies. Overall, from these results we conclude that the metastability of δ-phase Pu due to Ga is dependent on the decoupling of the Pu 5f-6d states in order for the Pu 6d states to hybridize with the Ga 4p states.

Supplementary Materials: The following are available online at http://www.mdpi.com/2076-3417/10/21/7628/s1, Figure S1: Partial density of states for (a) anti-ferromagnetic and (b) non-magnetic configurations for pure δ-Pu, and Figure S2: Partial density of states for non-magnetic configuration in 0.926 at. % Ga δ-Pu structure.

Author Contributions: S.C.H. and F.J.F. conceived the study. S.C.H. performed the electronic-structure calculations and wrote the original paper. F.J.F. reviewed the work and provided contributions to the analysis of the results, interpretation, discussions, and conclusions. All authors have read and agreed to the published version of the manuscript.

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