

A Density Functional Theory Study on Induced Covalent Short Bond Maximization on U in Pu-Ga Alloys and Extrapolation to the ζ -Pu-U Phase

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Understanding the effects of the radioactive decay of ²³⁹Pu due to its daughter products, U and He, on the phase stability of δ -Pu has been a long outstanding problem. While many Pu aging studies have focused on He ingrowth and its effects of void swelling, minimal studies have focused on U, even though significant amount of lattice damage will occur from the U recoil energy. It is well-known that U is a δ -phase destabilizer and thus using density functional theory, a systematic study of U defect calculations has revealed the fundamental role of U impurities in affecting the overall electronic structure of δ -Pu-Ga alloys and the complexity of Pu-U alloys in general (Figure 1). The calculations imply that U induces short bonds that enhance covalency in the δ -Pu lattice which competes with the Ga stabilization mechanism [1]. In addition, the migration of U within the δ -Pu-Ga alloys induces local distortions thus migrating as a multi-complex defect regardless of diffusion mechanism. U-vacancy migration yielded an activation energy of 1.27eV, where U-substitutional with neighboring Pu interstitial to a U octahedral interstitial site was slightly lower at 1.25eV. Therefore, the DFT results imply that the U atom can diffuse via either mechanism, although the formation energy to form the U-substitutional with neighboring Pu interstitial is 1.08eV lower in energy than a U-substitutional with first nearest neighboring Pu vacancy with formation energy of 0.04eV and 1.12eV, respectively. Interesting, the energy difference is the same energy required to form a Pu monoclinic monovacancy defect [2], where the U-vacancy defect resembled the same local distortions (Figure 2).

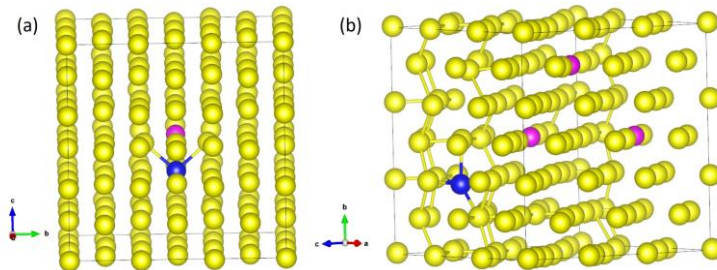


Figure 1: Ionic relaxed structures of (a) 0.926 at.% Ga of the U atom at first nearest neighbor distance from Ga and of (b) 2.778 at. % Ga of U octahedral at third nearest neighbor to the Ga atom. Pu atoms are yellow, U atoms are blue, and Ga atoms are purple.

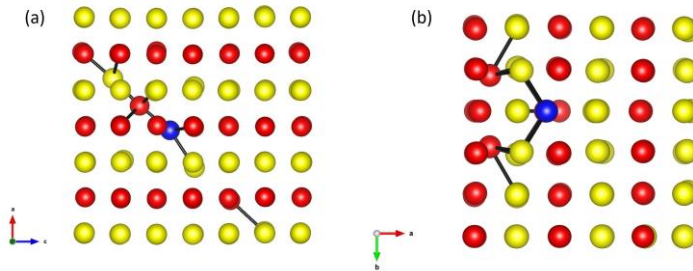


Figure 2: Migration of (a) interstitially mediated and (b) vacancy mediated U migration. The Pu anti-ferromagnetic arrangement is shown by spin-up (yellow) and spin-down (red), and the U atom is blue. Short Pu-Pu bonds <3.0Å are denoted by black.

We use these conclusions to extrapolate our findings to the ζ -Pu-U phase as defined by Lawson et. al [3] to distinguish the atomic lattice sites of the U and Pu atoms within this structure (Figure 3). Supporting evidence comes from random alloy modeling suggesting a significant U-U bonding interaction energy relative to weaker Pu-Pu interaction energy and a nearly nonexistent U-Pu interaction across the ζ -Pu-U composition range, but no evidence for short range order. Spin-polarized DFT calculations for the extrapolated ζ -phase were performed where the Pu atoms were treated in an anti-ferromagnetic arrangement, which was based on two criteria: (1) The first criteria that needed to be satisfy was that the spin-up and spin-down are determined when the Pu-Pu bond was $>2.8\text{\AA}$, followed by the second criteria of the Pu-Pu bonds at $2.8\text{\AA} < x < 2.95\text{\AA}$. After volume and ionic relaxation, where the cell shape remained constrained, the crystal structure underwent a percent difference of 3.35% in volume ($a_0 = 10.566\text{\AA}$ versus $a_{\text{expt}} = 10.685\text{\AA}$) and some bonds were slightly expanded or contracted (Figure 3). Therefore, this extrapolated version of the ζ -phase based on the induced covalent short bonding by a U defect observed in the δ -Pu-Ga alloys appears to be stable according to density functional theory calculations. Heat of formation and the electronic structure will be discussed further.

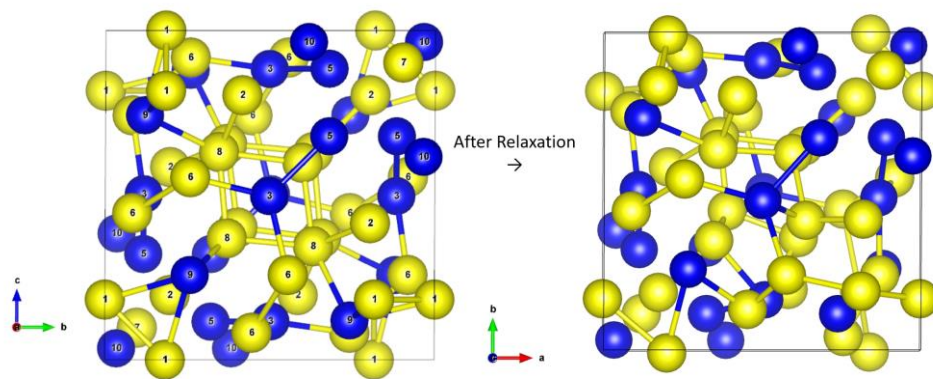


Figure 3: Left image is the hypothesized ζ -Pu-U structure as defined by Lawson et al. [2], where the U atoms are denoted in blue and Pu atoms are denoted in yellow. Right image shows the DFT volume and ionic relaxed structure.

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References:

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2. Hernandez, S.C., et al., *Spin density stabilization of local distortions induced by a monovacancy in delta-Pu*. Physical Review Materials, 2018. **2**(8): p. 085005.
3. Lawson, A.C., et al., *Structure of [zeta]-phase plutonium-uranium*. Acta Crystallographica Section B, 1996. **52**(1): p. 32-37.