



LAWRENCE  
LIVERMORE  
NATIONAL  
LABORATORY

# Atomic-volume variations of (alpha)-Pu alloyed with Al, Ga, and Am from first-principles theory

P. Soderlind, A. Landa, W. G. Wolfer

January 11, 2007

JOURNAL OF COMPUTER-AIDED MATERIALS DESIGN

This document was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor the University of California nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or the University of California, and shall not be used for advertising or product endorsement purposes.

# **Atomic-volume variations of $\alpha$ -Pu alloyed with Al, Ga, and Am from first-principles theory**

**Per Söderlind, Alex Landa, and William G. Wolfer**

**Physics and Advanced Technologies Directorate, Lawrence Livermore National  
Laboratory, University of California, PO Box 808, Livermore, CA 94550, USA**

## **Abstract**

First-principles methods are employed to calculate the ground-state atomic densities (or volumes) of  $\alpha$ -Pu alloyed with Al, Ga, and Am. Three configurations for the alloying atom are considered. (i) It is located at the most open and energetically most favorably site. (ii) It is located in the least open site. (iii) It is randomly distributed within the  $\alpha$ -Pu matrix. When alloyed with Al or Ga,  $\alpha$ -Pu behaves similarly, it expands considerably for configurations (ii) and (iii), while for (i) only small changes of the density occurs. Interestingly, for Am the alloying effects are quite different from that of Al and Ga. Small expansion is noted for the ordered configurations (i) and (ii), whereas for the disordered (iii), only insignificant changes of the density take place. The bonding character is thus differently influenced in Pu by the addition of Al and Ga on one hand and Am on the other. This is consistent with the view that Al and Ga stabilize the  $\delta$  over the  $\alpha$  phase in Pu by a different mechanism than Am, as has been discussed in recent publications.

**Keywords:** actinide alloys and compounds; crystal structure; computer simulations.

## 1. Introduction

At atmospheric pressure plutonium metal exhibits six crystal structures upon heating [1] from low temperatures to the melting point, see Fig. 1 [2]. The least dense phase,  $\delta$ -Pu, has a 25 % larger volume than  $\alpha$ -Pu and is thermodynamically stable at temperatures between 593 and 736 K. The ground-state  $\alpha$  phase is rather brittle due to its complex monoclinic crystal structure and the  $\delta$  phase is generally preferred. In order to extend the stability range of  $\delta$ -Pu to lower temperatures, plutonium is alloyed with a small amount of, for example, Al or Ga. Small amounts of Am is also always present as a byproduct of the radio-active decay that takes place in Pu. These three elements stabilize the  $\delta$  phase particularly well in a wide temperature and concentration range. The exact mechanism for this stabilization is not known, however. Recently it was proposed that Am stabilizes  $\delta$ -Pu by lowering the order-disorder magnetic transition temperature [3] whereas for both Al and Ga this effect was shown to be less significant, suggesting another physical origin of the stabilization process. Instead, the stabilization of the  $\delta$  phase over the  $\alpha$  phase may include alloying effects on the latter, which are different for Al and Ga on one hand, and Am on the other.

In this paper, we illuminate the stabilization process in Pu by computing the density in  $\alpha$ -Pu as a function of the alloy component Al, Ga, and Am. For this purpose we employ two complementary computational techniques: (i) the exact muffin-tin orbital method (EMTO) incorporated with the coherent potential approximation (CPA) to treat the compositional disorder and (ii) an all-electron full-potential linear muffin-tin orbital method (FPLMTO) that accounts for all relativistic effects in Pu, including spin-orbit

coupling and orbital polarization. Pertinent details of computation methods are described in Section 2. The results of the density-functional calculations are presented in Section 3. Lastly, in Section 4, we offer discussion and conclusion.

## 2. Computational techniques

The EMTO calculations are performed using a scalar-relativistic, spin-polarized Green's function technique based on an improved screened Korringa-Kohn-Rostoker method, where the one-electron potential is represented by optimized overlapping muffin-tin (OOMT) potential spheres [4, 5]. Inside the potential spheres the potential is spherically symmetric and it is constant between the spheres. The radii of the potential spheres, the spherical potentials inside the spheres, and the constant value from the interstitial are determined by minimizing (i) the deviation between the exact and overlapping potentials, and (ii) the errors coming from the overlap between spheres. Within the EMTO formalism, the one-electron states are calculated exactly for the OOMT potentials. As an output of the EMTO calculations, one can determine the self-consistent Green's function of the system and the complete, non-spherically symmetric charged density. Finally, the total energy is calculated using the full charge density technique [6]. For the electron exchange and correlation energy functional, the generalized gradient approximation (GGA) is adopted [7]. The calculations are performed for a basis set including valence *spdf* orbitals and the semicore *6s*, *6p* states, whereas the core states are recalculated at each iteration. For the total energy of random substitutional alloys, the EMTO is combined with the CPA [8].

The “full potentials” in FPLMTO refers to the use of non-spherical contributions to the electron charge density and potential [9]. This is accomplished by expanding charge density and potential in cubic harmonic inside non-overlapping muffin-tin spheres and in a Fourier series in the interstitial region. We use two energy tails associated with each basis orbital and for Pu’s semi-core  $6s$ ,  $6p$  states and valence states ( $7s$ ,  $7p$ ,  $6d$ , and  $5f$ ) these pairs are different. With this ‘double basis’ approach we use a total of six energy tail parameters and a total of 12 basis functions per atom. Spherical harmonic expansions are carried out through  $l_{max}=6$  for the bases, potential, and charge density. As in the case of the EMTO method, the GGA is used for the exchange-correlation approximation [7].

EMTO and FPLMTO calculations are performed for the antiferromagnetic (AF) optimized configuration [10,11] of the monoclinic lattice where the equivalent atoms have the anti-parallel spins. This magnetic configuration appears to have the lowest energy and becomes the ground state for  $\alpha$ -Pu [11,12]. For comparison, some calculations are performed with spin degeneracy enforced as a constraint, representing a non-magnetic assumption.

### 3. Results.

Figure 2 shows the 16-atom unit cell of the  $\alpha$ -Pu. This structure has eight non-equivalent lattice sites that are labeled according to the standard enumeration in the  $\alpha$  structure [13]. The two blue atoms in Fig. 2 are of “type 1” and the two red of “type 8”. The atoms of these two types (1 and 8) are of particular importance because they occupy the minimal (1) and maximal (8) Voronoi-cell volumes in  $\alpha$ -Pu [14]. Notice in Fig. 2, that the red atoms of type 8 appear to have more empty space around them than the other

atoms, whereas the blue atoms of type 1 are located in a higher-density space of the unit cell. We study a configuration of 15 Pu and 1 alloying atom, which occupies either of these two sites. The concentration of Pu in this cluster is 15/16, i.e., 93.75 %. In order to investigate random effects of the alloying atoms in the monoclinic lattice of  $\alpha$ -Pu, the  $\text{Pu}_{93.75}\text{Ga}(\text{Al},\text{Am})_{6.25}$  disordered alloy is also considered.

In Tables 1, 2, and 3, we show the FPLMTO and EMTO calculated atomic volumes, relative to pure  $\alpha$ -Pu, for Al, Ga, and Am atoms replacing the type 1 and type 8 atoms in  $\alpha$ -Pu, respectively. These calculations are anti-ferromagnetic, except the FPLMTO-NM calculations that are forced to be non-magnetic. Within the EMTO technique, also the corresponding concentration, disordered systems atomic volumes are calculated. Notice that the FPLMTO and EMTO techniques, although vastly different, actually produce almost identical results for Al and Ga in  $\alpha$ -Pu (Table 1 and 2). For Am, the numerical results show the same trend while the actual numbers are larger for the EMTO method. Technically, the Pu-Am calculations are more difficult because of the fact that Am spin polarize and perturb the magnetic configurations of  $\alpha$ -Pu, whereas this is not the case for Pu-Al and Pu-Ga. The fact that a non-magnetic treatment of  $\alpha$ -Pu yields too small equilibrium volume and too large bulk modulus is well known [11]. Nevertheless, this limitation appears to be less important for the Pu-Ga and Pu-Am systems, with some greater errors for the Pu-Al system.

Now, comparing the results for Pu-Al, Pu-Ga, and Pu-Am, we realize that Al and Ga behave rather similarly in the  $\alpha$  phase of Pu, as opposed to Am. The most obvious evidence of this is seen in the disordered calculations. For Al and Ga there is a rather substantial volume expansion of the  $\alpha$  phase, the so-called  $\alpha'$  phase, which for Ga is

consistent with recent measurements [15]. This is not the case for the  $\alpha$ -Pu-Am alloy, which display no expansion at all. The ordered FPLMTO calculations suggest only modest expansion, while the EMTO method predicts somewhat larger expansion for Am replacing both type 1 and 8 Pu.

### 3. Discussion and conclusion.

Sadigh and Wolfer [11] defined the  $\alpha'$ -phase of the Pu-Ga system as a random mixture of all eight  $\alpha_i$ -Pu<sub>1-x</sub>Ga<sub>x</sub> substitutional variants obtained via diffusionless martensitic transformation from the Ga containing  $\delta$ -Pu structure. This scenario is usually realized when the transformation takes place at the martensitic start temperature and occurs during the shortest possible transformation time. The theoretical treatment best corresponding to this situation is obtained within the disordered-alloy approach. The results described above suggest a strong expansion of the  $\alpha$  phase when formed this way from an Al or Ga stabilized  $\delta$ -Pu sample. Quite opposite behavior is detected when Al or Ga is substituted by Am. In this latter case, no expansion of  $\alpha$ -Pu is predicted. This is at first sight a counterintuitive result, as Al and Ga metals have smaller atomic volume (16.6 and 19.6 Å<sup>3</sup>) and Am a larger atomic volume (29.3 Å<sup>3</sup>) than that of Pu (20.0 Å<sup>3</sup>). I.e., alloying with a smaller component (Al or Ga) causes here an expansion, while alloying with a larger component (Am) results in no expansion. The reason for this could be obscure electronic-structure effects or simply because the geometry is very important for the equilibrium atomic volume. For instance, Pu itself expands when transforming from the monoclinic structure ( $\alpha$ ) to the close-packed phase ( $\delta$ ) (see Fig. 1). Am, the next

neighbor to Pu in the Periodic Table, likewise collapse when transformed from its ground-state close-packed structure to a monoclinic geometry [16].

In summary, with modern density-functional methods incorporated with accurate treatment of compositional disorder, we have been able to illuminate the nature of the bonding in  $\alpha$ -Pu alloyed with the good  $\delta$ -phase stabilizers, Al, Ga, and Am. We have also shown that Am behaves quite different in  $\alpha$ -Pu compared to that of both Al and Ga. The electronic structure of Am, in the Pu matrix, is much more similar to Pu than either Al or Ga. Consequently, the perturbation on the atomic volume and the overall bonding is much less when  $\alpha$ -Pu is being alloyed with Am, compared to Al and Ga.

### **Acknowledgements**

This work was performed under the auspices of the US Department of Energy by the University of California Lawrence Livermore National Laboratory under contract W-7405-Eng-48.

### **References:**

1. Hecker, S.S., Harbur, D.R., and Zocco, T.G., Prog. Mater. Sci., 49 (2004) 429.
2. Young, D.A., Phase Diagrams of the Elements, University of California Press, Berkeley, 1991.
3. Landa, A. and Söderlind, P., J. Alloys and Compounds, 354 (2003).
4. Vitos, L., Phys. Rev. B, 64 (2001) 014107.
5. Vitos, L., In Recent Research and Development in Physics, Transworld Research Network Publisher, Trivandrum, India, 2004, pp. 103-140.

6. Kollar, J., Vitos, L., and Skriver, H.L., In Dreysse, H. (Ed.), *Electronic Structure and Physical Properties of Solids: The Uses of the LMTO Method*, Lecture Notes in Physics, Springer, Berlin, 2000, pp. 85-113.
7. Perdew J.P., Chevary, J.A., Vosko, S.H., Jackson, K.A., Pederson, M.R., Singh, D.J., Fiolhais, C., *Phys. Rev. B*, 46 (1992) 6671; Perdew, J.P., Burke, K., and Ernzerhof, M., *Phys. Rev. Lett.*, 77 (1996) 3865.
8. Vitos, L., Abrikosov, I.A., and Johansson, B., *Phys. Rev. Lett.*, 87 (2001) 156401.
9. Wills, J.M., Eriksson, O., Alouani, M., and Price, D.L., In Dreysse, H. (Ed.), *Electronic Structure and Physical Properties of Solids: The Uses of the LMTO Method*, Lecture Notes in Physics, Springer, Berlin, 2000, pp. 148-167.
10. Söderlind, P., *EuroPhys. Lett.*, 55 (2001) 525.
11. Sadigh, B., Söderlind, P., and Wolfer, W.G., *Phys. Rev. B*, 68 (2003) 241101.
12. Söderlind, P. and Sadigh, B., *Phys. Rev. Lett.*, 92 (2004) 185702.
13. Zachariasen, W.H. and Ellinger, F., *Acta Crystallographica*, 16 (1963) 777.
14. Sadigh, B. and Wolfer, W.G., *Phys. Rev. B*, 72 (2005) 205122.
15. Faure, Ph., Klosek, V., Genestier, C., Baclet, N., Heathman, S., Normile, P., and Haire, R., In Sarrao, J.L., Schwartz, A.J., Antonio, M.R., Burns, P.C., Haire, R.G., and Nitsche, H. (Eds.), *Actinide – 2005 Basic Science, Applications and Technology*, MRS Symposium Proceedings, Vol. 893, MRS, Warrendale, PA, 2005, pp. 223-232.
16. Söderlind, P. and Landa A., *Phys. Rev. B*, 72 (2005) 024109.

## Figure Captions

Figure 1. The experimental phase diagram of plutonium [2].

Figure 2. The monoclinic  $\alpha$ -Pu structure [13]. Type 1 and 8 have the colors red and blue, respectively.

**Table 1.** Calculated equilibrium atomic volume, in  $\text{\AA}^3$ , for the Pu-Al system, relative to  $\alpha$ -Pu. All calculations are performed for the ground-state anti-ferromagnetic configuration, except the FPLMTO-NM, which are constrained to be non-magnetic.

Method	$\text{Pu}_{15}\text{Al}_1(8)$	$\text{Pu}_{15}\text{Al}_1(1)$	$\text{Pu}_{93.75}\text{Al}_{6.25}$
FPLMTO	- 0.13	0.70	-----
FPLMTO-NM	0.11	0.28	-----
EMTO	- 0.13	0.80	0.90

**Table 2.** Calculated equilibrium atomic volume, in  $\text{\AA}^3$ , for the Pu-Ga system, relative to  $\alpha$ -Pu. All calculations are performed for the ground-state anti-ferromagnetic configuration, except the FPLMTO-NM, which are constrained to be non-magnetic.

Method	Pu <sub>15</sub> Ga <sub>1</sub> (8)	Pu <sub>15</sub> Ga <sub>1</sub> (1)	Pu <sub>93.75</sub> Ga <sub>6.25</sub>
FPLMTO	0.15	0.59	-----
FPLMTO-NM	0.17	0.41	-----
EMTO	0.14	0.60	0.68

**Table 3.** Calculated equilibrium atomic volume, in  $\text{\AA}^3$ , for the Pu-Am system, relative to  $\alpha$ -Pu. All calculations are performed for the ground-state anti-ferromagnetic configuration, except the FPLMTO-NM, which are constrained to be non-magnetic.

Method	Pu <sub>15</sub> Am <sub>1</sub> (8)	Pu <sub>15</sub> Am <sub>1</sub> (1)	Pu <sub>93.75</sub> Am <sub>6.25</sub>
FPLMTO	0.13	0.06	-----
FPLMTO-NM	0.0	0.0	-----
EMTO	0.49	0.62	0.0

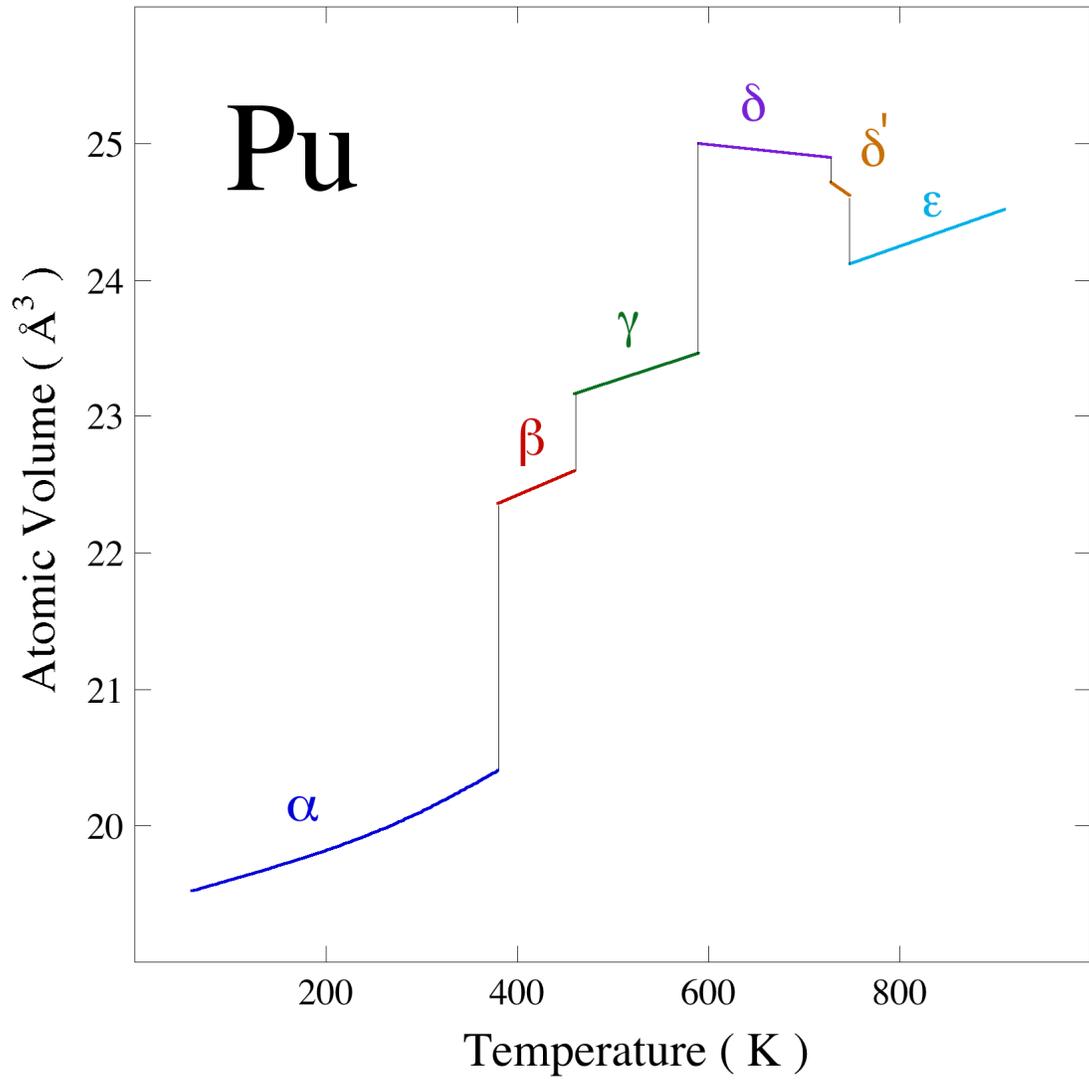
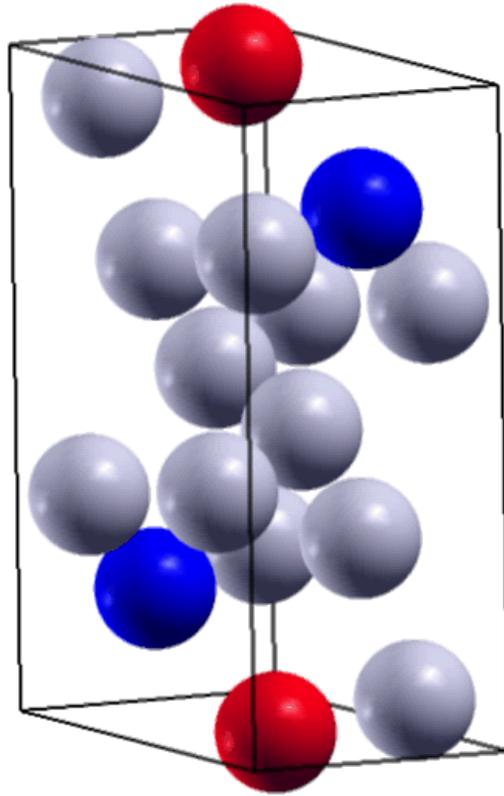


Figure 1.



**Figure 2.**