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Density-functional calculations of α-Pu–Ga(Al) alloys

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Abstract

First-principles methods are employed to study the ground-state atomic volumes of α-Pu–Ga(Al) alloys. It is shown that a random distribution of Ga(Al) atoms in the monoclinic lattice of α-Pu results in a maximum expansion of this lattice and creation of the so-called α′-Pu phase. Any kind of ordering of Ga(Al) atoms on the monoclinic lattice results in a shrinking of the lattice constant while the ordered α_8-(Pu–Ga(Al)) configuration yields the smallest lattice constant which is very close to that of pure α-Pu. In addition, energetics of the ordered (unrelaxed and relaxed) and disordered configurations is discussed.

Keywords: Actinide alloys and compounds; Crystal structure; Computer simulations

1. Introduction

At atmospheric pressure plutonium metal exhibits six crystal structures upon heating from room temperature to the melting point. The least dense phase (δ-Pu, fcc) has a 25% larger volume than the ground-state (α-Pu, monoclinic) phase and is thermodynamically stable at temperatures between 593 and 736 K. In order to extend the stability of δ-Pu to ambient temperatures, plutonium is alloyed with a small amount of so-called 'δ-stabilizers', for example, Ga or Al. The α-phase has no equilibrium solubility with any of these δ-stabilizers, but upon cooling of the δ-Pu–Ga(Al) alloys, under certain conditions, Ga(Al) atoms can be randomly trapped in the monoclinic lattice causing its expansion. An expanded monoclinic Pu–Ga(Al) phase is referred to as the "α′-phase". It was suggested [1] that the enhanced volume of α′-Pu is solely due to the random distribution of Ga(Al) solutes in the monoclinic lattice and the unexpanded α-Pu lattice can be restored if the solute atoms are forced to move into preferred positions, e.g. during annealing. It was also observed [2] that the cell volume for the α′-phase, formed under pressure, depends on the rate of the pressure increase: a rapid pressure increase traps solute atoms in random positions leading to a larger cell volume, while a slow pressure increase would give time for solutes to diffuse to preferred sites which leads to a smaller cell volume.

Recently, Sadigh and Wolfer [3] performed plane-wave pseudopotential calculations for a variety of super-cell configurations based on the α-Pu monoclinic structure. They found that the volume for the α′-Pu–Ga unit depends on which of its eight non-equivalent sites [4] (see below) gallium atoms order due to the tempering. They also found that the smallest unit cell volume corresponds to distribution (ordering) of Ga atoms over the so-called 'type 8 sites' in the monoclinic lattice (the authors called this configuration 'the α_8-$\mathrm{Pu}_{1-x}\mathrm{Ga}_x$ substitutional variant'). However, this configuration gives specific ordering of the solutes atoms on the selected sites and a disordered Pu–Ga alloy cannot be easily considered within the super-cell technique used in Ref. [3].

In the present paper 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. Pertinent details of computation methods are described in Section 2. The results of the density-functional calculations of α-Pu–Ga(Al) alloys are

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presented in Section 3. Lastly, in Section 4, we offer discussion and conclusion.

2. Computational details

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 [5,6]. 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 [7]. For the electron exchange and correlation energy functional, the generalized gradient approximation (GGA) is adopted [8]. 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 [9].

The "full potentials" in FPLMTO refers to the use of non-spherical contributions to the electron charge density and potential [10–12]. 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 7f) 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.

EMTO and FPLMTO calculations are performed for the antiferromagnetic (AF) optimized configuration [13,14] 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 α-Pu [13–15].

Finally, in order to get a realistic energy for the α-Pu–Ga(Al) configuration, with a gallium (aluminum) atom ordered on the specific site of the monoclinic lattice, the relaxed configuration is obtained from calculating forces within the plane-wave pseudopotential technique as implemented in the VASP code [16].

3. Results

Fig. 1 shows the 16-atom unit cell of the α-Pu (this picture is borrowed from Ref. [3]). This structure has eight non-equivalent lattice sites that are labeled according to the standard enumeration in the α structure [4]. We study configuration of 15 Pu and 1 Ga(Al) atoms with Ga(Al) atom occupies sites 1 or 8. The concentration of Pu and Ga(Al) in this cluster is 93.75% and 6.25%, respectively. In order to study random effects of Ga(Al) atoms in the monoclinic lattice of α-Pu, the $Pu_{93.75}Ga(Al)_{6.25}$ disordered alloy is also considered.

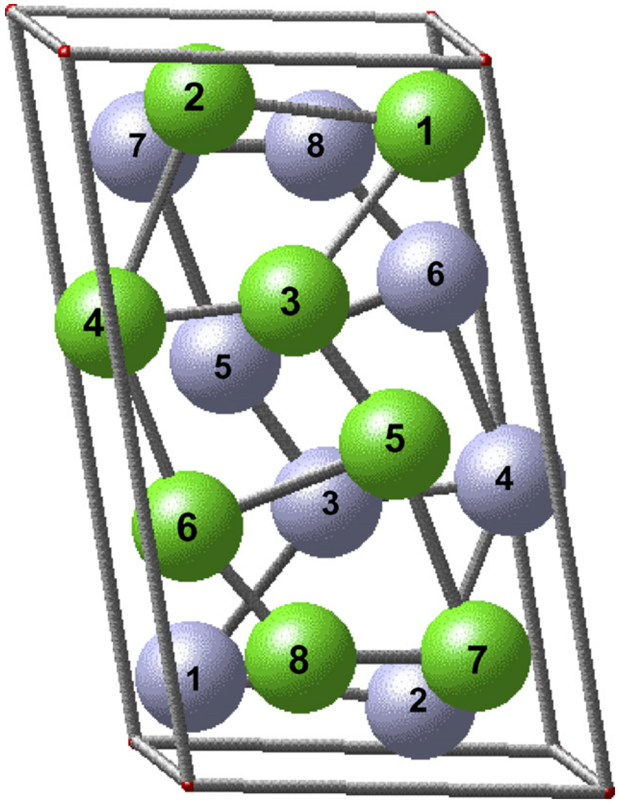

Fig. 1. The α-Pu structure [3]. The blue and green planes are related by an inversion symmetry operation. The atoms in each plane are labeled by numbers 1–8 according to the standard enumeration (Ref. [4]) in the α structure. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of the article.)

Table 1 shows the equilibrium atomic volume of the Pu–Ga system when a gallium atom occupies sites 1 or 8 of the monoclinic lattice. This table also shows the equilibrium atomic volume of the $Pu_{93.75}Ga_{6.25}$ disordered alloy with Ga atoms randomly distributed in the monoclinic lattice. Calculated equilibrium volume of pure α-Pu is 20.12 and 19.70 Å^3 for the EMTO and FPLMTO methods, respectively, which is in good agreement with results of recent measurements at room temperature (19.99 Å^3) [17]. However, for convenience, the equilibrium volume of pure Pu is considered as the reference point and

Table 1
Calculated equilibrium atomic volume, in Å^3, for Pu–Ga system

Method	Pu	$Pu_{15}Ga_1$		$Pu_{93.75}Ga_{6.25}$ disordered alloy
		Ga occupies site 8	Ga occupies site 1	
FPLMTO	0	0.15	0.59	–
EMTO	0	0.14	0.60	0.68

The equilibrium volume of pure Pu is taken as 0 (the reference point).

Table 2
Calculated equilibrium atomic volume, in Å^3, for Pu–Al system

Method	Pu	$Pu_{15}Al_1$		$Pu_{93.75}Al_{6.25}$ disordered alloy
		Al occupies site 8	Al occupies site 1	
FPLMTO	0	−0.13	0.70	–
EMTO	0	−0.13	0.80	0.90

The equilibrium volume of pure Pu is taken as 0 (the reference point).

set equal to zero. Thus, Table 1 shows only a relative value (increment) of the atomic volume of the Pu–Ga system. As one can see from this table, the random distribution of Ga atoms gives the largest unit cell compared to when Ga atoms are ordered in the specific sites (1 or 8). Notice, in the case of the $Pu_{15}Ga_1$ (site 8) configuration, the equilibrium volume is slightly larger than that of pure α-Pu, which is in excellent agreement with resent XRD measurements [2]. One should also mention that the results of EMTO and FPLMTO calculations for the Pu–Ga system are almost identical for both ordered configurations and this suggests robustness in the density-functional approach.

Table 2 shows the equilibrium atomic volumes of the Pu–Al system and its layout is identical to Table 1. Again, the solute (Al) expands the α-Pu lattice by randomly occupying its sites. However, contrary to the previous case, the equilibrium volume of the $Pu_{15}Al_1$ (site 8) configuration is slightly smaller than that of pure α-Pu.

Our calculations reveal that the energy of the unrelaxed $Pu_{15}Ga_1$ (site 8) configuration is lower than the energy of the $Pu_{15}Ga_1$ (site 1). On the other hand, the EMTO calculations show that the energy of the unrelaxed $Pu_{15}Ga_1$ (site 8) configuration is about 4.5 mRy/atom higher than that of the disordered $Pu_{93.75}Ga_{6.25}$ solution. However, the plane-wave pseudopotential calculations establish that if Ga atoms are allowed to relax either in the position 8, or position 1, the system decreases its energy on average 8.3 mRy/atom. Similar results are obtained for the Pu–Al system. Thus, ordering of the solutes (Ga or Al) on sites 8 brings the α-Pu–Ga(Al) system to the energetically favorable state.

4. Discussion and conclusion

Sadigh and Wolfer [3] defined the α′-phase of the Pu–Ga system as a random mixture of all eight α_i-$Pu_{1-x}Ga_x$ substitutional variants obtained via diffusionless martensitic transformation from the Ga containing δ-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. Fig. 2, also borrowed from Ref. [3], illustrates their interpretation of the expanded molar volume of the α′-Pu phase based on the calculated partial molar volume (PMV) of Ga in the different lattice sites of the monoclinic structure (this plot shows results of the plane-wave pseudopotential calculations obtained for clusters containing 16, PMV Ga 1/15, and 32, PMV Ga 1/31, atoms, and this notation was missed from the caption for this plot in Ref. [3]). Clearly, the experimental value of the partial molar volume of Ga in α-Pu for infinite diffusion and un-tempered condition is always larger than the same property calculated for each of the eight different sites in the monoclinic structure and can not be simply reproduced as a random mixture of all the α_i-$Pu_{1-x}Ga_x$ substitutional variants as suggested in Ref. [3]. However, the present calculations, performed within the EMTO-CPA formalism with its ability to treat compositional disorder, clearly show that the random distribution of the solutes (Ga or Al) in the α-Pu lattice results in a maximum its expansion in comparison with each of eight substitutional variants. Upon tempering (heating up to moderate temperatures or a slow pressure increase), the solute atoms will diffuse to the energetically favorable α_8-$Pu_{1-x}Ga(Al)_x$ substitutional variant with a subsequent excess volume collapse. Finally, as soon as the solutes atoms, which have no equilibrium solubility in α-Pu, will be driven from the monoclinic lattice of plutonium metal, e.g. by segregating to defect sites such as the vacancy clusters, grain boundaries, dislocations, etc., the original size of the unit cell of pure α-Pu will be recovered.

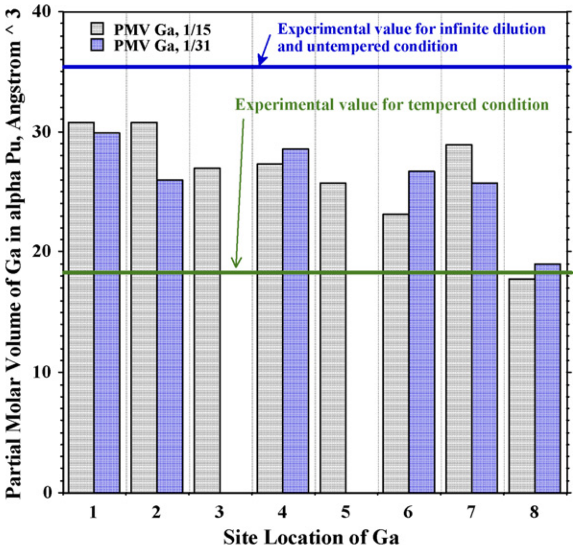

Fig. 2. The partial molar volume of Ga in the different lattice sites of the α-Pu structure [3] (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of the article.)

In summary, with modern density-functional methods incorporated with accurate treatment of compositional disorder, we have been able to illuminate the nature of the expanded α′-phase of plutonium metal.

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