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X-ray diffraction study of δ-stabilized plutonium alloys under pressure

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ABSTRACT

Previous extensive studies of the δ → α′-phase transformation induced by temperature and/or by pressure in δ-stabilized plutonium alloys indicate strong dependence on parameters such as solute type, solute distribution, chemical impurities, kinetics, thermodynamic path….The present paper reports results obtained on two Pu–2.3at.%Ga binary alloys differing by solute homogenization treatment and studied under pressure by *in situ* by X-ray diffraction in diamond anvil cells. The γ′-phase appears as an intermediate phase during the δ → α′-phase transformation. In cored samples, unexpanded α′-phase is formed at the beginning of the transformation, from domains with low solute content, and expanded α′-phase subsequently forms (from domains with higher solute content) as the transformation progresses with the pressure increase.

1. Introduction

Pu shows, due to a complex electronic structure, six allotropic solid phases at ambient pressure under temperature [1]. The face centred cubic δ-phase (*fcc* form, S.G. *Fm3m*), stable between 315 and 457 °C, is by far the most studied and it still remains a great challenge for physicists especially because of the difficulty in describing accurately the 5*f* electronic structure and therefore bonding properties [1–4]. Alloying plutonium with gallium, aluminium, cerium or americium stabilizes the δ-phase at room temperature. It was only until recently that a worldwide consensus has developed regarding the stability of this phase in the Pu–Ga system [1]: the δ-phase would be metastable at ambient temperature and would undergo extremely slow (over a period of approximately 10,000 years) eutectoid decomposition towards a mixture of α-plutonium (monoclinic form, S.G. $P2_1/m$) and the compound Pu_3Ga (*fcc* form, S.G. *Fm3m*). However, although theoretical approaches are developed and thus enlighten our understanding of the mechanisms for stabilization [5], more studies are needed to fully understand a delicate system (that is very sensitive to parameters such as pressure, temperature and chemical composition) which presents in addition, due to self-irradiation, continuous evolution of its composition (chemical and isotopic) and physical properties [1,6].

The δ → α′-phase transformation (the prime denotes solute atoms trapped in the α lattice), which can be triggered by increasing pressure or lowering temperature has been studied extensively [1,6–16], revealing often intermediate phases. Progress is being made in its characterization and description but given the variety of behaviours (resulting for instance to a many parameters dependence such as solute type, solute distribution, chemical impurities, kinetics, thermodynamic path…) additional experiments are still needed for a better understanding.

In previous works [12,13], three alloys (Pu–8at.%Am, Pu–15at.%Am and Pu–2at.%Ga) were studied under pressure by X-ray diffraction (XRD) in diamond anvil cells and revealed: (i) a pressure-induced softening of the δ-phase and (ii) an intermediate γ′-phase (a face-centred orthorhombic structure, S.G. *Fddd*, similar to γ-Pu [17]) across the δ → α′-phase transition. We report here *in situ* X-ray diffraction results that reveal subtle features occurring during the δ → α′-phase transition in two Pu–2.3at.%Ga alloys differing by solute homogenization treatment.

2. Experimental

In order to study the effect of gallium segregation on the compressibility and on the δ → α′-phase transformation, two freshly cast plutonium–gallium samples with gallium content of 2.3 at.% underwent heat treatment at 460 °C to partially homogenize the gallium distribution and to ensure that the samples were only δ-phase. These samples were referred as ‘cored’ as gallium segregation was still observed. An additional heat treatment of 200 h at 460 °C was performed on one of the cored samples to nearly fully homogenize the gallium distribution. This sample is referred as ‘homogenized’.

Pieces of plutonium alloys were then rolled at room temperature down to 30–35 μm thickness and annealed (1 h/360 °C) to restore metallic structure (elimination of both structural defects caused by self-irradiation and stress induced by rolling). Thereafter resulting foils were electropolished in a cooled bath (−7 °C) composed of 90% ethylene glycol and 10% nitric acid to remove surface

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oxides. These foils were then cut with a scalpel to obtain square like shaped samples of 100 μm edge and about 25 μm thickness, ready to be loaded within DACs.

Experimental details regarding DAC loading, pressure measurement, and XRD acquisition are similar to the ones described in [18]. Argon was used as a pressure transmitting medium and pressure was determined by measuring the fluorescence of four rubies (Al_2O_3:Cr^{3+}) put close to each sample [19].

In the following, we present XRD results established on four samples up to 2 GPa by performing small pressure steps (50–100 MPa) once to twice a day: two Pu–2.3at.%Ga homogenized samples (referred as h1 and h2) measured 1 to 2 months after heat treatment and two Pu–2.3at.%Ga cored samples (referred as c1 and c2) measured 2 years after heat treatment. Aging effects are considered neglected in this work.

3. Results and discussion

3.1. $\delta \rightarrow \alpha'$-phase transformation in Pu–2.3at.%Ga

Fig. 1 represents Rietveld refinements obtained for homogenized Pu–2.3at.%Ga sample when crossing the $\delta \rightarrow \alpha'$ transition. As it has been recently reported the transformation is not direct but involves the γ'-phase [12]. The alloy began to transform at $P_S = 0.44(2)$ GPa and two to three phases were then observed to coexist up to $P_E = 1.2(1)$ GPa: the δ-phase, the γ'-phase and the α'-phase. The same trend was observed for the cored Pu–2.3at.%Ga samples, the pressure of transformation being slightly lower ($P_S = 0.30(2)$ GPa and $P_E = 1.1(1)$ GPa). This is coherent with the fact that domains with low gallium content transform at lower pressure. Our results are consistent with Hecker's dilatometry measurements [1] which show a transformation at 0.30 GPa for a gallium content of about 1.8at.%, and a transformation at 0.44 GPa for a gallium content of about 2.4at.%.

γ'-phase was never observed as pure. That suggests it is a metastable structural intermediate phase occurring during the $\delta \rightarrow \alpha'$ transformation. This result also rises the question about the exact nature of this pressure induced structural transformation and in particular regarding its martensitic character, the transformation being a two-stage transformation: $\delta \rightarrow \gamma' \rightarrow \alpha'$.

After having reached 0.8 GPa in sample c2 (Fig. 2a), a pressure for which the transformation is not complete (γ'-phase and α'-phase coexist), the sample has been decompressed down to ambient pressure and XRD was realized one day and fifteen days after the pressure release. Analysis shows that δ-, γ'- and α'-phases coexist, which implies that δ-phase formed during the decompression (Fig. 2b). As it is established that δ-phase never forms after decompression at room temperature when the $\delta \rightarrow \alpha'$ transformation has been completed (the phase transformation being irreversible for such alloy's composition), this suggests that δ-phase had formed from γ'-phase. Furthermore, Fig. 2 reveals that amounts of α'-phase diminishes (94% at 0.8 GPa and 80% after pressure release) together with γ'-phase (6% at 0.8 GPa and 2–3% after decompression) while δ-phase grows (0% at 0.8 GPa and 17% after decompression): this implies that part of the α'-phase transformed to γ'-phase during decompression.

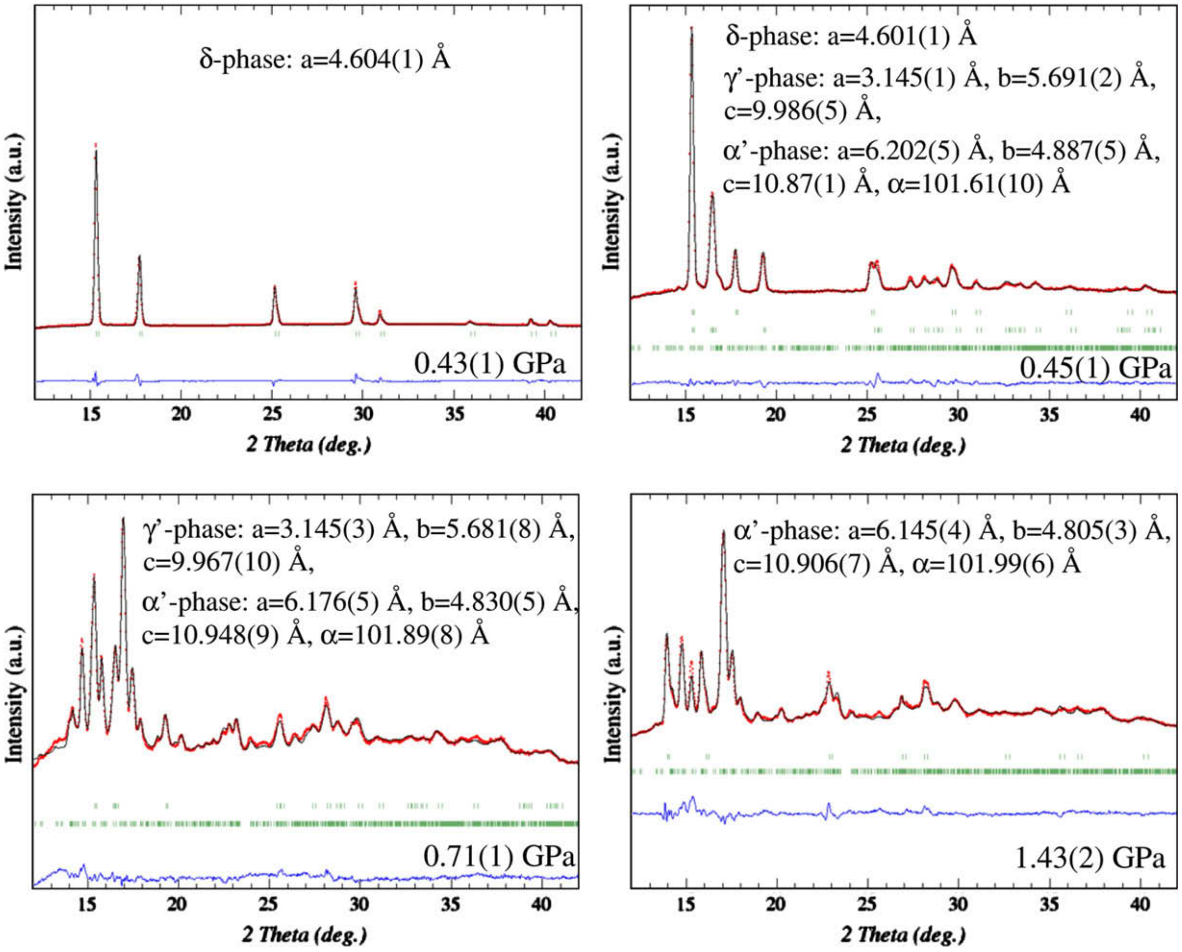
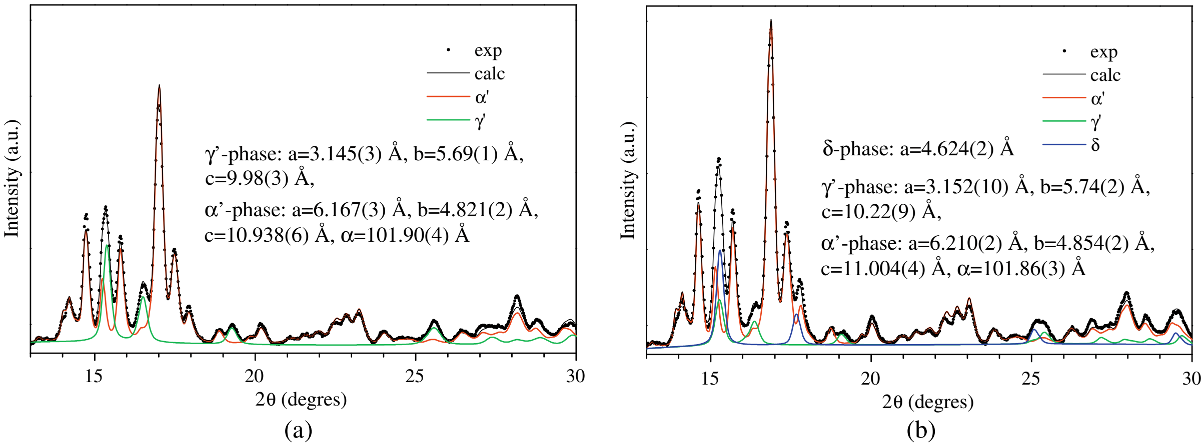
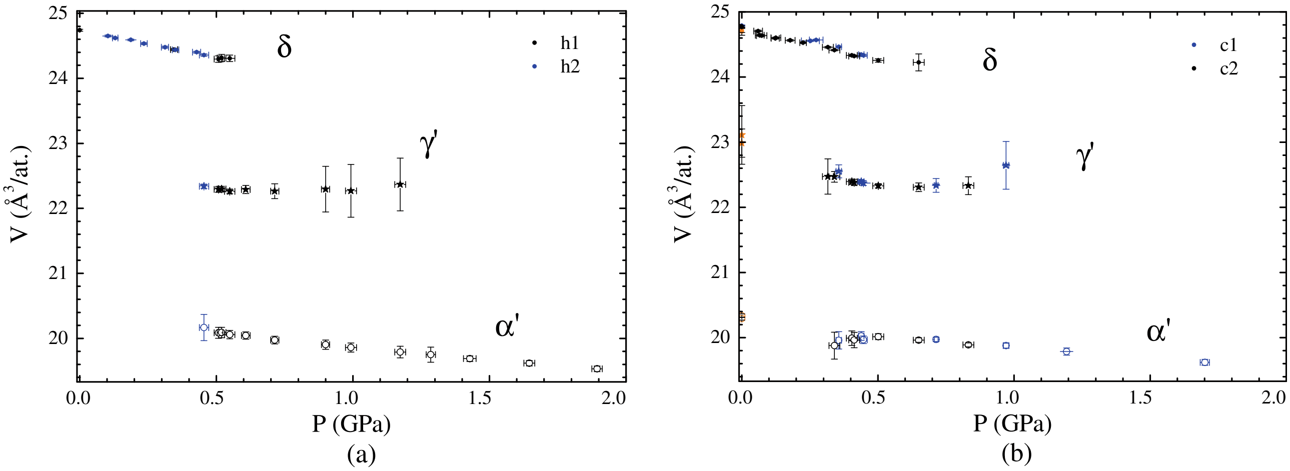


Fig. 1. Rietveld refinements of homogenized Pu–2.3at.%Ga alloy under pressure and at room temperature. Points represent the experimental data, the upper continuous line is the calculated pattern and the lower continuous line is the difference profile. The hkl positions of the different phases are represented by the lower vertical lines.



(a) (b)

Fig. 2. Room temperature Rietveld refinements of cored Pu–2.3at.%Ga alloy (sample c2): (a) at 0.83(2) GPa and (b) at ambient pressure fifteen days after pressure release. Data were normalised to exposure time. Contribution of each phase is shown.



(a) (b)

Fig. 3. Room temperature atomic volumes measured when increasing pressure for: (a) homogenized Pu–2.3at.%Ga and (b) cored Pu–2.3at.%Ga. Data in red (colour inline) correspond to sample c2 after pressure release.

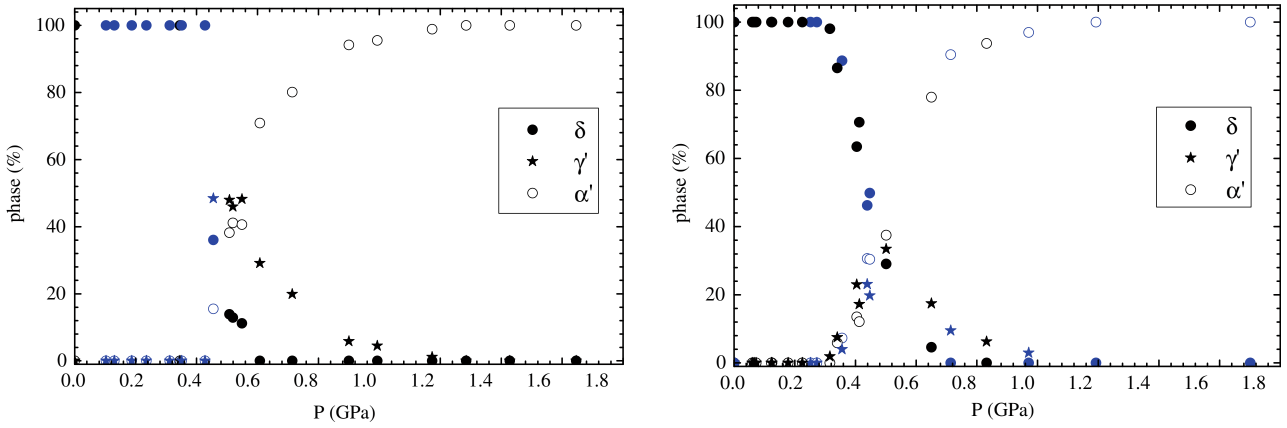
The observation of an intermediate phase corroborates other works in Pu–Ga alloys subjected to pressure. Hecker reported that Pu–Ga alloys, subjected to isostatic pressure, appeared to transform directly from δ → α′ with a possible trace of γ′-phase [1]. Goldberg [7] and Deloffre [8] also found the γ′-phase to be an intermediate for low-gallium alloys, and which disappeared very rapidly at room temperature. Very recently, Schwartz et al. also observed the δ → γ′ → α′ pressure-induced transformation path in diamond anvil cell experiments on Pu–3.3at.% Ga alloys [6]. In addition, these authors report line broadening from the initial δ-phase which they interpret as unresolved line splittings of a δ′-phase, a body-centred-tetragonal structure that is similar to the high-temperature δ′-phase observed in pure plutonium. We also observe in our measurements line broadening for the δ-phase when pressure is increased, the peak FWHM (Full Width at Half Maximum) increase remaining lower than 12%. A FWHM decrease is even observed in the homogenized samples just before the transformation. More significant line broadening was recently measured during the cooling-induced δ → δ + α′ transformation on a highly homogenized Pu2at.%Ga alloy and was interpreted by the authors in terms of anisotropic microstrain resulting from the stress induced by the high density difference between the δ- and α-phases [10].

γ′-phase is also reported on the Pu–Am system: in Pu–8at.%Am the γ′-phase is observed as an intermediate phase [13], while for higher americium content (Pu–15at.%Am, Pu–20at.%Am and Pu–24at.%Am) γ′-phase is observed as a pure phase [12,20] which pressure stability domain increases as the solute content increases. Shall we generalize and conclude that γ′-phase must be an intermediate phase during the transformation in δ-stabilized plutonium alloys?

Zukas's studies on Pu–2at.%Al [11] showed that the method of transformation greatly affects the sequence of transformation products: γ-phase appears as an intermediate phase when mechanical polishing is performed, while the β′-phase is the intermediate phase when hydrostatic compression is applied. Moreover the δ → α′ transformation promoted by low-temperature treatment is direct both in low-gallium alloys (1.7 < [Ga(at.%)] < 2.5) and in Pu–2at.%Al [1,10], while Pu–1at.%Ga shows γ′-phase [1]. Furthermore, Pu–Am alloys do not transform by low-temperature treatment [13–14,21].

Blobaum and co-workers hypothesized, in order to explain α′-phase amounts formed after different thermodynamic paths (or "conditioning treatments"), that the cooling-induced δ → α′ transformation involves embryos of the thermodynamically stable α-phase, which subsequently nucleate α′ particles upon cooling [9]. However, there has been, until now, no direct evidence for such embryos [6,22].

It is interesting to note that recent theoretical works predict that the δ → α′ transformation occurs via an intermediate hexago-



(a) (b)

Fig. 4. Phase quantification versus pressure for: (a) homogenized Pu–2.3at.%Ga (h1 data in black and h2 data in blue) and (b) cored Pu–2.3at.%Ga (c1 data in blue and c2 data in black). (colour online).

nal structure [15–16]. However, the fact that the MEAM potential used in Gröger's calculations does not reproduce accurately the low symmetry structures of Pu (α- and β-phase) could bias the predictions. More progress is still needed in this very challenging field which implies that one should be able to accurately describe, with the same model, all the known phases of plutonium.

Atomic volumes and phase quantifications derived from Rietveld analysis are presented versus pressure in Fig. 3 and Fig. 4, respectively. The good agreement between data sets for each type of alloy (cored/homogenized samples) indicates good reproducibility of the measurements. However slight discordances are observed for δ-phase atomic volumes of cored samples, the evolution of these volumes with pressure being in addition more complex than the one observed for the homogenized samples.

Evolution of atomic volumes reveals large volume collapses: 8.2% between δ- and γ′-phases, and 9.5% between γ′- and α′-phases. The huge volume shrinkages may be linked to sudden pressure induced delocalization of 5*f* electrons and a subsequent increase of the 5*f* electron participation in the metallic bonding. Such structural transitions should imply large negative stresses within the sample, which seems to affect strongly the γ′-phase as it will be presented later.

Among main differences between cored and homogenized samples one can note:

- the pressure of transformation (already discussed before),
- the maximum amount of γ′-phase, which is smaller in the case of cored samples (50% for homogenized samples versus 35% for cored samples),
- an abrupt transformation start for homogenized samples. Note that for pressures higher than 0.5 GPa, that is when γ′-phase amount decreases, homogenous and segregated samples possess the same length changes,
- different evolution for α′-phase volumes when transformation begins. This is discussed below.

Knowing, for each phase, the phase amount and the corresponding atomic volumes (Figs. 3 and 4), length changes can be calculated as a function of pressure. These data (Fig. 5) agree qualitatively with dilatation measurements of Hecker on homogenized Pu–1.7at.%Ga and Pu–2.5at.%Ga. This indicates that (microscopic) length changes derived from XRD yield the major behaviour measured at a macroscopic level. It is not possible from such a continuous length change to guess that an intermediate phase is present during the transformation. This is why *in situ* phase characterization by XRD is essential to improve the understanding of such complex transformation. Other complementary structural analysis techniques like X-ray absorption spectroscopy or diffuse scattering analysis could also complete such investigation.

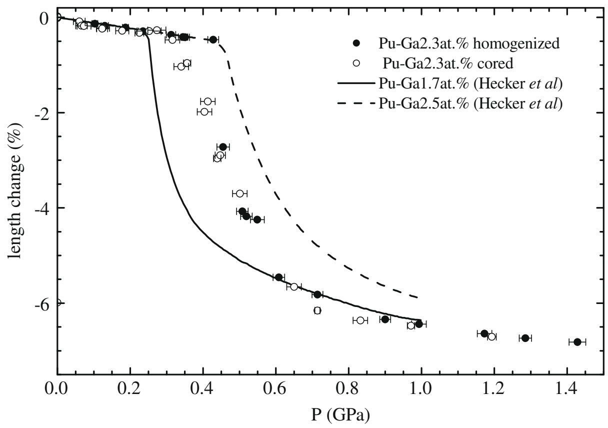


Fig. 5. Room temperature length changes measured when increasing pressure. Data for Pu–2.3at.%Ga are calculated from XRD measurements while data for Pu–1.7at.%Ga and Pu–2.5at.%Ga (homogenized 200 h at 450 °C) correspond to measurements (from [1]) with a Bridgman-type pressure dilatometer.

Quantitative differences observed between XRD data and dilatation measurements may originate from kinetics, segregation, macroscopic particularities (grain size, non diffracting impurities or phases...) and from an analysis point of view, to the phase quantification accuracy. It would be very valuable, when possible to generalize such comparisons (microscopic information/macroscopic measurements) which yield global view of the system.

3.2. Isothermal (300 K) compressibility of δ-phase for Pu–2.3at.%Ga

As already stated above, δ-phase atomic volumes obtained with cored samples show more fluctuations than homogenized samples (Fig. 6): c1 and c2 data sets reveal discrepancies, although very good agreement was observed for ambient pressure cell parameters. More experiments would be needed to corroborate the results and understand this behaviour.

Vinet fit [23] performed over homogenized Pu–2.3at.%Ga data (only data below 0.5 GPa were considered in order to limit eventual stress induced artefacts when δ-domains become minatory)

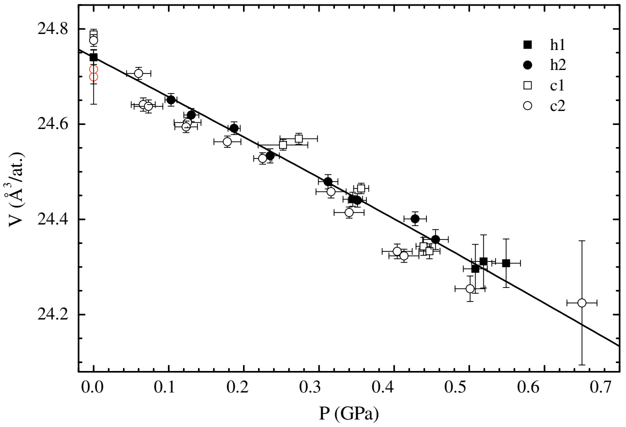


Fig. 6. Room temperature atomic volumes of δ-phase measured when increasing pressure for homogenized and cored Pu–2.3at.%Ga. Continuous line represents Vinet fit over homogenized samples.

leads to: $V_0 = 24.74(1)$ Å^3, $B_T = 30(1)$ GPa and $B'_T = -6(5)$. Although large uncertainties are obtained when deriving B'_T (due to a narrow pressure range in the fit), it appears to be negative or close to zero. That indicates softening under compression, a behaviour which may result from pressure induced delocalization of plutonium's 5*f* electrons [12–13], and which was predicted by the statistical mechanical model proposed by Lawson [24], based on a two-level 'Invar'-like electronic structure.

3.3. Isothermal (300 K) compressibility of γ′-phase for Pu–2.3at.%Ga

Very good agreement is observed between different data sets for γ′-phase atomic volumes (Fig. 7). It can be noticed that volumes increase for pressures higher than 0.55 GPa. This phenomena may result from large negative stresses within the sample arising from huge volume difference (9.5%) between γ′ and α′-phases. Furthermore, γ′-phase amount decreases in this pressure domain while α′-phase amount increases and is higher than 60% (Fig. 4).

Vinet fit was realized over low pressure data (i.e. pressures inferior to 0.5 GPa) in order to avoid stress induced artefact data. One obtains $B_T = 13(2)$ GPa when V_0 and B'_T are set to 23.05 Å^3 and 5, respectively (Fig. 7). Note that these parameters should be taken only as estimates as the fit was over a narrow pressure range and measured ambient volumes are associated to high uncertainties.

It should be pointed out that γ′-phase atomic volumes depend much, at a given pressure, on alloy composition. For instance, Pu–8at.%Am and Pu–15at.%Am data presented in [12] have volumes higher than Pu–2.3at.%Ga ones, and the higher the americium content is the higher the volumes are. Thus, these results comfort the idea that γ′-phase is an *expanded* γ-phase with solute atoms trapped in the plutonium lattice.

3.4. Isothermal (300 K) compressibility of α′-phase for Pu–2.3at.%Ga

α′-phase atomic volumes (Fig. 8) differ between homogenized and cored Pu–2.3at.%Ga alloys, up to at least 0.5 GPa. Atomic volumes for cored samples are lower, and even show "unphysical" evolution, that is an expansion when pressure is increased. That can be explained by the fact that the first δ (or γ′?) domains which transform towards α′-phase under pressure are the low gallium content domains [1]. Indeed, knowing that the α′-unit cell expansion induced by gallium (at a given pressure and temperature) increases with gallium content [1], lower expansion is expected for first formed α′-phase domains than for lately formed domains. As a consequence, as the transformation processes and until it is completed, the mean atomic volume measured for α′-phase increases as pressure is increased. Such an evolution is not observed anymore for sufficient sample homogenization, which is the case of our "homogenized" samples.

The fact that very first points measured for cored samples lie exactly on the pure plutonium curve (Fig. 8) indicates that first formed α′-phase domains are unexpanded. Do they correspond to α-phase? It appears that cell parameters of first formed α′-phase domains (between 0.3 and 0.5 GPa) in cored alloys differ from pure plutonium ones (Fig. 9): although parameters a are similar, b and monoclinic angle β are higher while c are smaller. These differences, attributed to the presence within plutonium matrix of gallium atoms, are solute concentration dependent. A striking behaviour is the evolution of parameter c: a shrinkage (compared to pure plutonium) is measured in very first α′-phase domains while an expansion is measured in lately formed domains. These results differ qualitatively from the cell parameter evolution versus gallium concentration, published by Hecker, which report only expansions [1]. Stress within first formed domains could affect cell parameters and thus explain differences.

α′-phase atomic volumes measured in the present work at ambient pressure (after pressure release with samples c1 and c2)

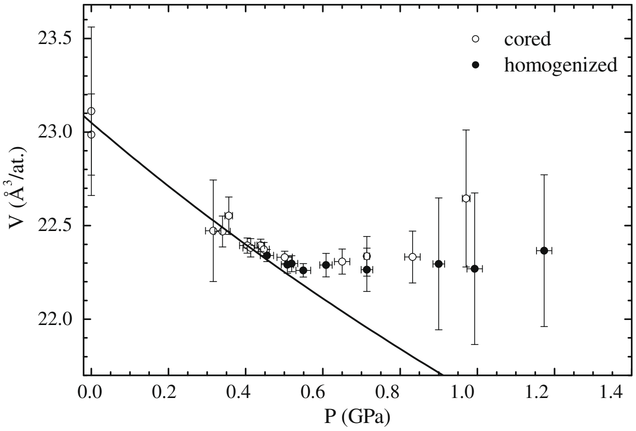


Fig. 7. γ′-phase atomic volumes versus pressure, measured at room temperature when increasing pressure, for homogenized and cored Pu–2.3at.%Ga. Data at ambient pressure were recorded for sample c2 after pressure release. Continuous line is a Vinet fit over data below 0.5 GPa.

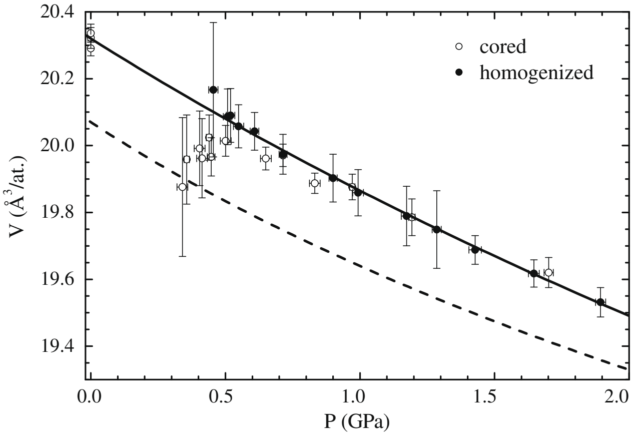


Fig. 8. α(α′)-phase atomic volumes, measured at room temperature when increasing pressure, for homogenized and cored Pu–2.3at.%Ga. Data at ambient pressure were recorded after pressure release for sample c2. Continuous line is a Vinet fit for homogenized alloys and dashed line is a Vinet fit derived for pure plutonium data (from [18]).

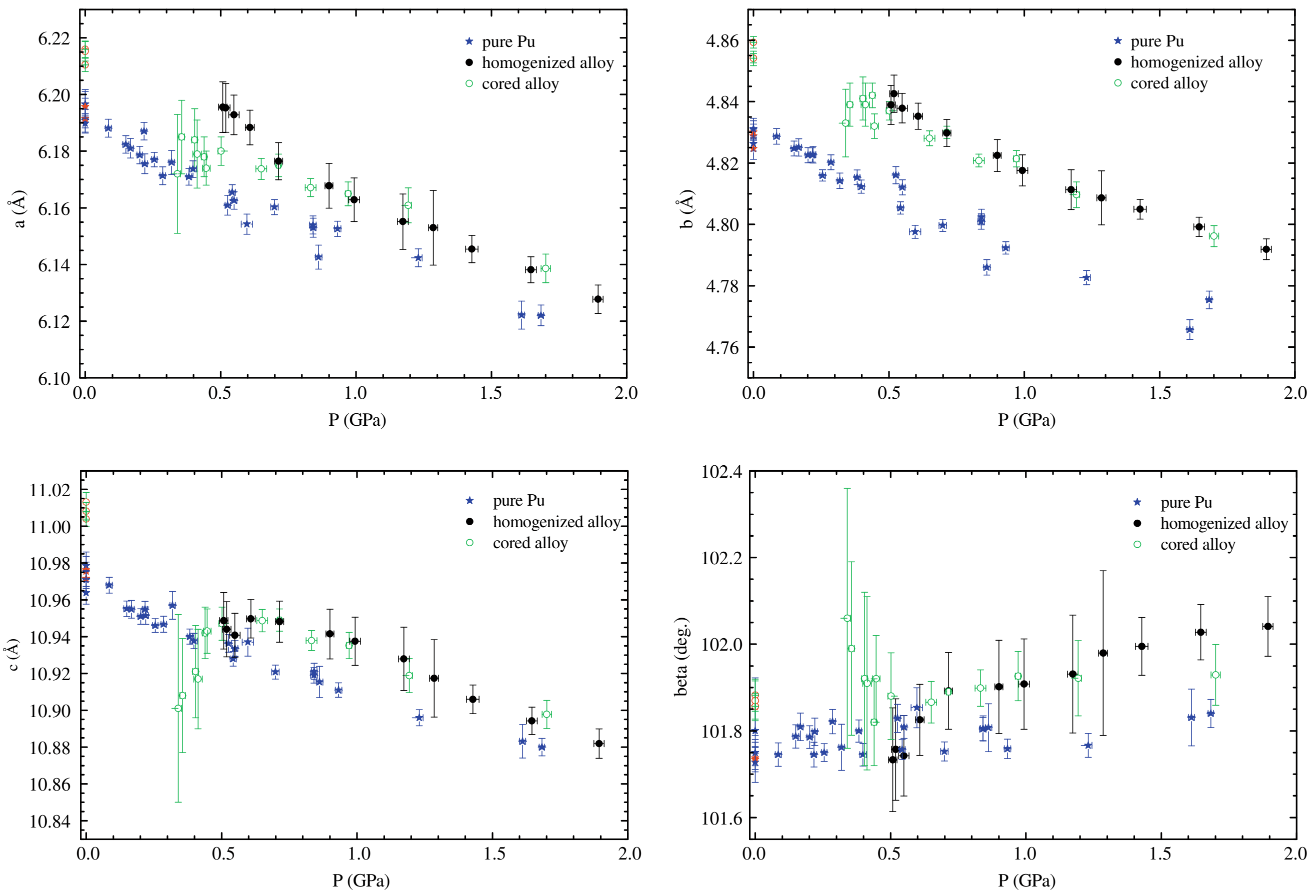


Fig. 9. Room temperature unit-cell parameters of α(α′)-phase measured when increasing pressure for homogenized Pu–2.3at.%Ga, cored Pu–2.3at.%Ga and pure plutonium data (from [18]). Data in red were obtained after pressure release (colour online).

range between 20.29 and 20.34 Å^3. Fixing V_0 to 20.32 Å^3, Vinet fit performed over homogenized samples in the α′-phase (Fig. 8) leads to $B_T = 40(1)$ GPa and $B'_T = 9(2)$. This set of parameters gives a good description of the alloy's compressibility, within the 0–2 GPa pressure range, as measured with a rate of pressure increase of 0.05–0.2 GPa/day. However it may not describe correctly the compressibility at higher pressures or for higher rates of pressure increase. Indeed, it has been observed, from several experiments performed on well homogenized δ-stabilized Pu alloys (Pu–Am and Pu–Ga), that the unit-cell volume for the α′-phase formed under pressure depends on the rate of the pressure increase [12]: for instance, a 0.7% difference was measured between two rates of pressure increase in a Pu–8at.%Am alloy at 1.2 GPa. This phenomena could be explained by Söderlind's first-principle calculations [25] which show how α′-phase volume expansion depends on solute atom position within the cell. Furthermore, the solute would move, with time, towards preferential sites inducing unit-cell shrinkage [1,12].

4. Conclusion

Two Pu–2.3at.%Ga binary alloys differing by solute homogenization treatment were studied under pressure by *in situ* XRD in diamond anvil cells. γ′-phase is shown to be an intermediate phase during the δ → α′-phase transformation. Unexpanded α′-phase is formed in cored samples at the beginning of the transformation from domains with low solute content. Expanded α′-phase subsequently forms as the transformation progresses with increasing pressure. The α′-phase volume, as measured with a rate of pressure increase of 0.05–0.2 GPa/day, is 0.9% higher than pure plutonium α-phase volume [18] at 2 GPa.

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