

The effect of pressure on phase-stability in the Pu–Ga alloy system

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Abstract

In examining and analyzing over three decades of research on the transformations involved in Pu–Ga alloys, it is clear that many incongruities and contradictions exist. New analysis shows that under certain processing conditions large amounts of a non-diffracting disordered state exists in Pu–Ga alloys, which I call the amorphous state. The amorphous state is certainly not an equilibrium state, but it can be formed under certain pressure conditions, and more surprisingly once formed can persist for extended times and temperatures. It is believed that the emergence of the amorphous state is closely linked to the 5f-electrons going into a bonding mode. Being a physical state, the amorphous state has distinct physical properties, meta-stabilities, and sensitivities to Ga content.

The existence of an amorphous state requires innovative new tools for identification and analysis. The density and compressibility data presented in this paper is one such tool for analyzing the amorphous state, but it requires other knowledge of the materials for proper analysis. Many studies point to radiation damage producing amorphous regions. New computer modeling studies show the existence of amorphous regions and Pu-rich interstitial defects in Pu–Ga alloys.

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1. Introduction

The face centered cubic (fcc) δ -phase with up to several atomic % Ga is unstable at all temperatures as the pressure is increased to just over 5 kbar. Under these conditions, the δ -phase has been reported [1,2] to transform to one of the more dense phases: α , β , γ , or ζ , depending upon the temperature. Pressure tends to favor the more-dense crystalline state in Pu, a metal which exists in more crystalline-states than any other metal. At temperatures above 500 °C the body centered cubic (bcc) ϵ -phase actually becomes amorphous (melts) as the pressure is increased. In this latter case, pressure favors the more-dense amorphous state over a less-dense crystalline state. By 1975 [3,4] John Wood and co-workers doing band structure calculations were able to examine the contribution of the 5f-electrons to bonding. Their calculations showed that as the Pu atoms move from their normal lattice position across the saddle point into an adjacent vacancy, the f-orbitals overlap in a bonding mode, causing a contraction of the lattice in the region of the vacancy.

The phenomenon can be described as local melting, since the central region of the activated state constitutes a small liquid “nucleus”, and the bonding processes are the same as those that cause the liquid Pu to be denser than the ϵ -phase.

More recent modeling efforts by Valone et al. [5] give very important insights into the phase-stability of the δ -phase in Pu–Ga alloys. In studying the effects of He in-growth in these alloys by the modified EAM (MEAM) formalism, they have shown that He bubbles may influence the phase transformation rates and permit formation of amorphous zones. They also note at higher cascade energies the large amorphous regions that form anneal very slowly relative to conventional fcc metals. The He bubbles can also drive the formation of Pu-rich interstitial defects in Ga-depleted regions. This model also predicts a tendency toward segregation in Pu–Ga alloys [6]. This work is extremely important and adds to our understanding of the possible mechanisms by which the δ -phase disorders as it moves to the equilibrium state of α -phase + Pu₃Ga. The pressure associated with the He bubbles may be responsible for accelerating disorder in the δ -phase.

Liquid Pu exists to what appears to be a very abnormally low temperature for the actinide series [7]. The effect of pressure is to make the liquid stable to even lower temperatures.

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The density of liquid Pu is greater than the density of the three high-temperature phases, δ , δ' , and ϵ quite possibly because the 5f-electrons are more easily accommodated in the liquid. At high pressures, the liquid crystallizes directly into the body centered monoclinic β -phase, bypassing all of these lower density phases. There is almost no volume change when the liquid crystallizes into the β -phase. There is considerable evidence that liquid metal poured into a constrained mold configuration never transforms to the δ' - and δ -phases during the cooling process [8]. If these low-density phases were to crystallize in this constrained environment, then considerable pressure would have to build up from the concomitant expansion. It is believed that this pressure prevents these lower-density phases from forming and the material remains in a higher-density phase during the cooling process.

In this paper I have tried to show why I believe that the conclusion some have reached concerning the existence of an amorphous state in Pu is not only correct but should cause a reexamination of many of our theories on phase relationships in the Pu alloys, particularly the Pu–Ga alloys under pressure. I do not believe that the amorphous state is easily produced in most normally processed Pu–Ga alloys or that it is an equilibrium state. Under the conditions of modest pressure, and phase instabilities the existence of the amorphous state is not only a possibility, but I believe it is a reality.

2. The amorphous state in a Pu–0.68 at.% Ga alloy

A Pu–0.68 at.% Ga alloy, well homogenized for 168 h at 440 °C in the δ -phase temperature region, and inert-gas cooled to RT, was observed by Zukas et al. [9,10] to have a density of 17.5 g/cm³. This density result was near expectations, since it was well known that this alloy did not contain enough Ga to fully stabilize the δ -phase down to RT. The X-ray diffraction results were however totally unexpected because only the α -phase was identified as being present, whereas our experience told us that

it would be impossible for an alloy with this Ga content to be all α -phase at this point. The micro hardness at 102 DPH, far below the hardness of the α -phase, was more consistent with the density data that indicated only partial transformation of the δ -phase to the α -phase. The researchers reporting this discrepancy had extensive experience in the X-ray diffraction field, and had previously been able to identify every phase of Pu in various other samples. Given its symmetry and strong diffraction lines, the fcc δ -phase is the most easily detected crystal structure in Pu and since the material was obviously in the δ -phase during the long homogenization period, it was a total surprise not to find any δ -phase in this specimen that should only be partially transformed to the α -phase during the cooling cycle to RT. Zukas had previously worked with alloys processed in a similar manner having slightly higher Ga contents and had easily identified α' -phase (expanded α -phase with entrapped Ga) and large amounts of the δ -phase by X-ray diffraction. This inconsistency was thoroughly investigated by Zukas and the results were even repeated after many intermediate treatments of the specimens followed by another simple homogenization and inert-gas cooling to RT. The results were also repeated on several other low-Ga alloy specimens. The implications of this discrepancy are enormous. Depending upon the density of the non-detected phase, it means that about half of the material is undetected if its density is near that of the δ -phase or even greater if the density of the undetected phase is greater than the δ -phase. These results left only two possible conclusions; either the crystallite size of the δ -phase had become extremely small and thus non-diffracting or the material was disordered and non-crystalline (amorphous). The conclusion reached by Zukas was that the undetected material is amorphous.

For slightly higher Ga-content alloys the microstructure, after a partial transformation to the α' -phase at a density near 17.5 g/cm³, consists of α' -phase needles in an untransformed δ -phase matrix [11] (Fig. 1). For this particular alloy, the microstructure seems much more broken up, with no long

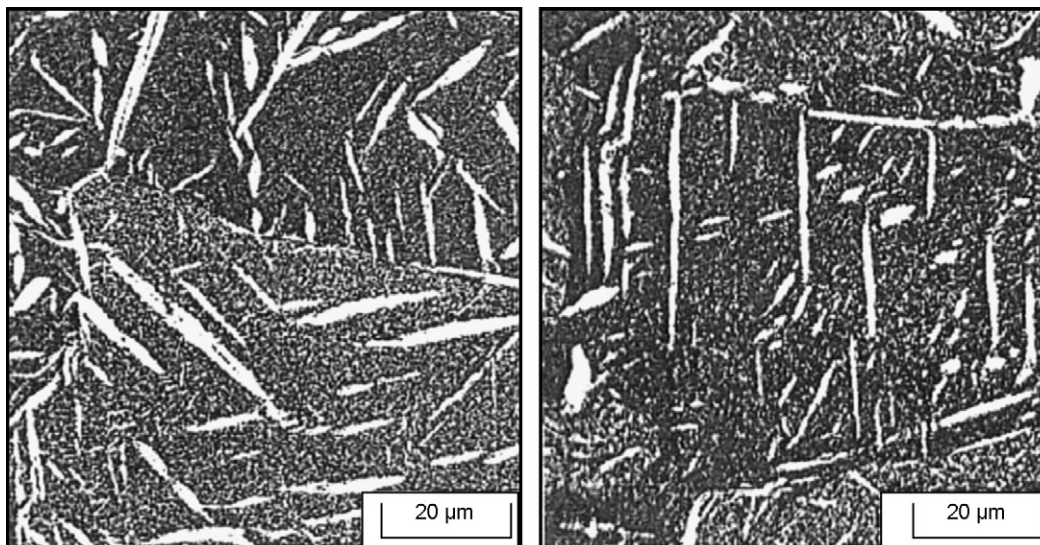


Fig. 1. Pu–1.7 at.% Ga homogenized alloy showing formation of α' -phase from subzero treatment. The α' -phase is the white needle like structure in a background of the δ -phase.

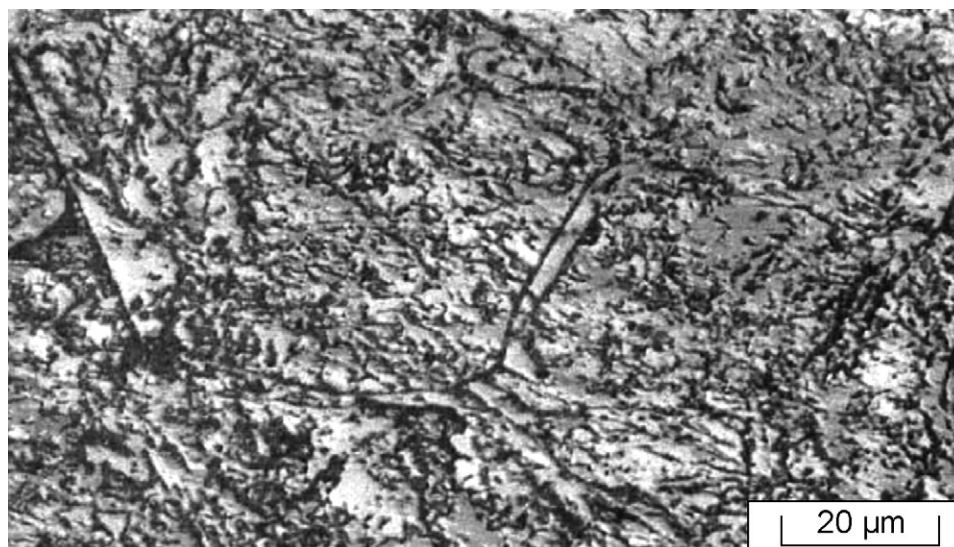


Fig. 2. Pu–0.68 at.% Ga alloy after air cooling to RT from a δ -phase homogenization at 440 °C for 168 h. Density of 17.5 g/cm³ indicates partial transformation of δ -phase. Only phase detected by X-ray diffraction is the α' -phase. The α' -phase appears as precipitates in a background of the amorphous state. The former δ -phase grain boundaries are still apparent.

α' -phase needles, although remnants of the former δ -phase grain boundaries are visible (Fig. 2). This smooth background phase is in fact non-diffracting and is therefore the amorphous state.

To study the behavior of this low-density non-crystalline phase, Zukas took a specimen of this alloy in the homogenized condition that had only been cooled to RT and heated it at ambient pressure to 180 °C and held it there for 3 h. From the volume change as calculated from the dilatometric traces, only the α' -phase showed evidence of transformation to the β -phase. This is an interesting result from two standpoints. First it shows that the amorphous state is stable to the high temperature of 180 °C and is now in equilibrium with the β -phase. Since the β -phase has almost no solubility for Ga, the Ga, which was entrapped in the α' -phase prior to its transformation to the β -phase, must go into solution in the adjacent amorphous state increasing the overall Ga content of the amorphous state. Upon cooling back to RT the Ga depleted β -phase transforms to the α -phase and the amorphous state remains, even though it now has a Ga content near 0.8 at.%. This result shows that the amorphous state, once formed, is still preferred over the δ -phase after a temperature cycle to 180 °C, even though the Ga content has been raised to about 0.8 at.%.

One other observation by Zukas concerning the amorphous state is quite interesting. He performed bend tests [12] on specimens of the Pu–0.68 at.% Ga alloy, with and without the amorphous state present. He prepared two different specimens having the same densities, 18.25 g/cm³ but with one containing the amorphous state and the other containing the δ -phase. The specimen that contained 49% α' -phase and 51% amorphous-state fractured at a bend angle of 7.4°, whereas the specimen with 42% α -phase and 58% δ -phase fractured at a bend angle of 19.9°. From extensive bend testing of specimens having only the α' - and δ -phases, Zukas was able to demonstrate that to a first order, the bend angle was directly related to the amount of α' -phase in the mixture. From Zukas' work these bend angles

would correspond to plastic elongations of about 1 and 7%, respectively for α' plus δ -phase mixtures. The only valid conclusion from these tests is that the amorphous state is much more brittle than the δ -phase, although it is impossible to separate the brittleness of the amorphous state from the brittleness of the transformation product of the amorphous state, since it is hard to imagine that the amorphous state remains unchanged throughout the test. It should be noted that the above comparison is somewhat flawed because in the first case he was bend testing an α' -phase + amorphous state mixture, whereas in the second case, he was testing an α + δ -phase mixture. The 255 °C treatment used on the second specimen would cause total rejection of Ga from the α' -phase. However the minor differences in ductility between the α' - and α -phase, is inadequate to explain the results observed.

3. Density and compressibility data

During the early 1970s, a series of experiments were conducted by the author on several Pu–Ga delta-phase alloys with Ga contents of 1.0, 1.7, 3.3, and 6.6 at.% Ga. Density and compressibility data were gathered for all of these alloys in the homogenized δ -phase state. The compressibilities were calculated from the longitudinal and transverse sound speeds measured on the samples at room temperature, and the densities were measured by the Archimedeian method. For the Pu–1.0 at.% Ga and Pu–1.7 at.% Ga alloys the room temperature densities and compressibilities were also measured after several pressure or thermal cycling treatments that produced phase mixtures with increased densities. These experiments were some of the first to try to understand what happens to the δ -phase alloy when it transforms under hydrostatic pressure. Some of the Pu–1.7 at.% Ga alloy specimens were also given β -phase and γ -phase heat treatments after the original pressure treatments. At the time of these experiments, there was limited understanding of the com-

plex transformations that occurred in these alloys due to pressure or low temperatures. X-ray diffraction results identified only two phases in these pressure or low-temperature transformed specimens, α and δ . No attempts were made to determine quantitatively the amounts of the two phases by X-ray diffraction. No thought was given to the possibility that the X-ray diffraction results may have missed detecting a non-diffracting phase.

The X-ray diffraction measurements of the α -phase identified in these pressure-transformed specimens showed that the α -lattice was expanded. All three axes of the monoclinic crystal structure were greater than those measured for the unalloyed α -lattice. We believed that the $\delta \rightarrow \alpha$ transformation was martensitic in nature and that all of the atoms shifted together from one crystalline site to another without diffusion. We quickly concluded that this orchestrated shift of atoms caused the Ga to be trapped in the α -lattice and that this artificial entrapment led to the expanded lattice.

When the densities and compressibilities were plotted on a graph it became apparent that the compressibilities for the mixed phase specimens were anomalously high. Since the compressibility of a two-phase mixture is equal to the sum of the compressibilities of each phase on a volume basis, it follows by the rule of mixtures law that the data points for mixtures of the two phases should fall on a straight line between the data points of the individual phases. Our results implied that the compressibility of one of the two identified phases was higher after the pressure cycle. We speculated that the expanded lattice of the α' -phase was perhaps more compressible than the normal α -phase. This theory however was slowly disproved as we learned that the compressibilities of phase mixtures with more and more

α' -phase began to converge on the compressibility of the normal α -phase. This behavior is reflected in Fig. 3 where we show three data points for the Pu–1.7 at.% Ga alloy pressurized to 10.3 kbar and two data points for a Pu–1.0 at.% Ga alloy pressurized to 6.3 and 10.3 kbar. These two sets of data points each have a separate line that passes through them with the lower terminus of each line being at the calculated density of the α' -phase containing 1.7 and 1.0 at.% Ga, 19.3 and 19.55 g/cm³, respectively. Interestingly the compressibility of the α' -phase for these two alloys and the compressibility of the pure α -phase are identical, showing that the compressibility of the α -phase is unaffected by the entrapped Ga. The two lines that we have drawn converge at a density near 17.1 g/cm³ and a compressibility of 0.041 GPa⁻¹. I believe this data point is representative of a non-diffracting phase, labeled as the amorphous state. We have already mentioned the Pu–0.68 at.% Ga alloy that had a density of 17.5 g/cm³ in which only the α' -phase was detectable by X-ray diffraction. I have noted in Fig. 3 where I believe this data point would lie, had we measured its compressibility.

If in actuality, we have a three-phase mixture as shown in Fig. 3, it follows that the plotted data points for the three-phase mixture will fall in the triangular space formed by connecting the three data points for these phases. As the phase mixture approaches being totally one phase, the data points for the mixtures should converge on the data point for that single phase. If we have a two-phase mixture consisting of an amorphous state and the α' -phase, as we go to higher and higher pressures, forming more and more α' -phase, we should see the data points converge on the data point for the α' -phase as shown in Fig. 3. There are two ways that we can calculate the relative

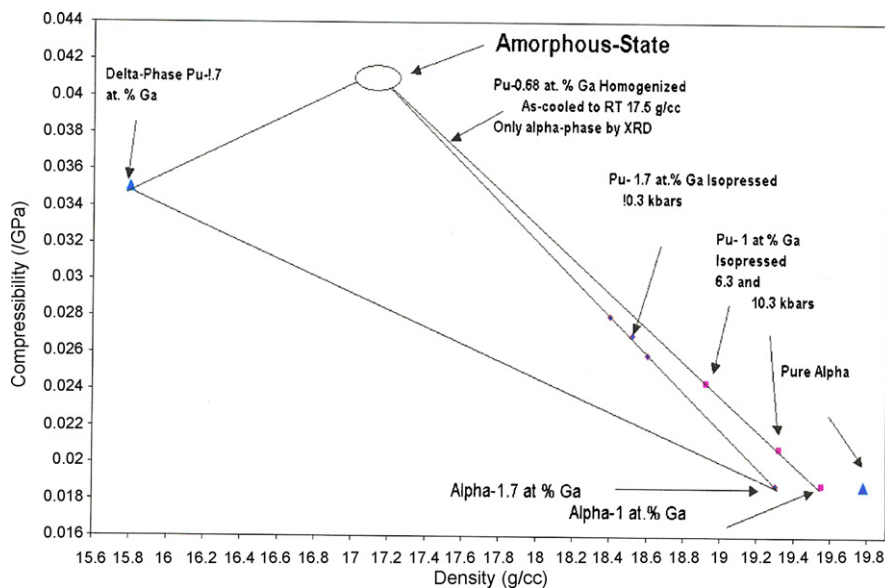


Fig. 3. Density and compressibility data showing data points for Pu–1.7 at.% Ga homogenized δ -phase, and mixed-phase data points for the same alloy after hydrostatic pressing for various times at 10.3 kbar. The later data points are connected with a line that also goes through the data point shown as the α' -phase with 1.7 at.% Ga at the known density of the α' -phase and at the same compressibility value that was measured for the pure α -phase at a density of 19.78 g/cm³. The two data points for the Pu–1.0 at.% Ga homogenized alloy hydrostatically pressed to 6.3 and 10.3 kbar are similarly connected with a line that terminates at the known density of the α' -phase with 1.0 at.% Ga and the same compressibility of the other α -phase data points. These two lines converge near a density of 17.1 g/cm³ and a compressibility of 0.041 GPa⁻¹ at the amorphous state. I have also indicated where I feel the data point for the Pu–0.68 at.% Ga homogenized alloy that was air cooled to RT would lie on this plot. Since the only phase detected by X-ray diffraction is the α -phase, the data point must be close to the line connecting the amorphous-state and the α -phase.

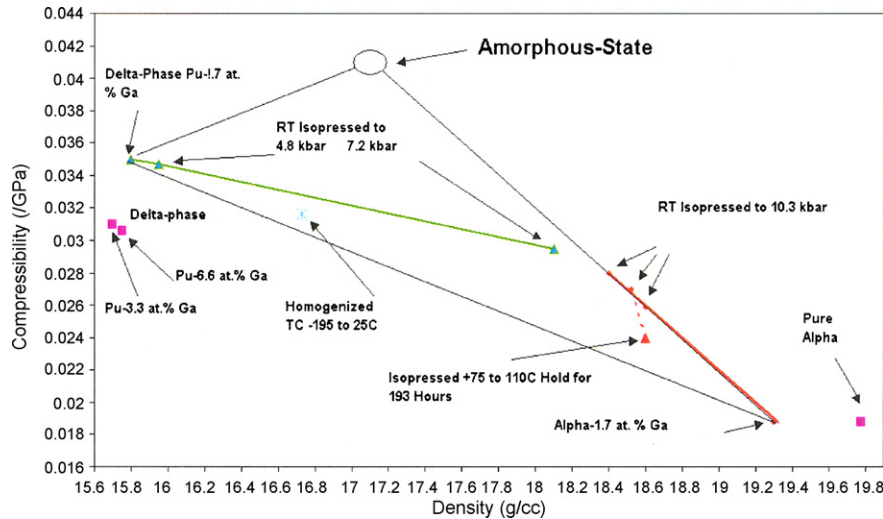


Fig. 4. Density and compressibility data taken at RT. There are four single-phase data points shown, the α -phase for unalloyed-Pu, and the δ -phase for Pu with 1.7, 3.3 and 6.6 at.% Ga. Three data points for the Pu–1.7 at.% Ga homogenized alloy hydrostatically pressed to 10.3 kbar at RT, with hold times at maximum pressure of 12, 30 and 60 min each. A linear line drawn through these three data points intersects the density value of the α' -phase with 1.7 at.% Ga at a compressibility of 0.0188 GPa^{-1} . The same compressibility measured for the pure α -phase. Two data points generated for this alloy hydrostatically pressed at lower pressures of 4.8 and 7.2 kbar can be connected with a linear line which also runs through the value obtained for the δ -phase containing 1.7 at.% Ga. The data point for a homogenized specimen that was thermal cycled between -195 and 25°C lies just below this line. The red triangle data point was measured after holding the specimen, that was previously hydrostatically pressed at 10.3 kbar (30 min) for 193 h at 75 – 110°C .

amounts of the amorphous state and the α' -phase for the data points shown. These calculations are only valid if we actually do have a two-phase mixture as we have postulated. Since we know the densities of the two phases, it is easy to calculate the weight fraction of these two-phases at any given mixture density. Using the lever rule, we can also calculate the relative amounts of the two phases directly off of the plot in Fig. 3. The calculations for the five mixed-phase data points are shown below:

Mixed-phase density (g/cm^3)	Density calculation		Lever rule calculation	
	α' -Phase	Amorphous	α' -Phase	Amorphous
18.40	62	38	60	40
18.52	67	33	65	35
18.60	71	29	69	31
18.92	76	24	75	25
19.32	91	9	91	9

The results from the two different calculations are in close agreement, and certainly add credence to our contention that the mixed-phase data points shown consist of only the two phases: the amorphous state and the α' -phase.

In Fig. 4 we show the triangle established above for the three phases in the Pu–1.7 at.% Ga alloy and also show two more data points for this alloy after pressure cycles to 4.8 and 7.2 kbar. These two data points can be connected with a line, which also runs through the data point obtained for the δ -phase containing 1.7 at.% Ga. This shows that one of the phases in these phase mixtures is the δ -phase. As the homogenized alloy is taken to higher and higher pressures, the δ -phase is transforming into a mixture of about 57% α' -phase + 31% amorphous state with 12% δ -phase remaining at 7.2 kbar. The Pu–1.7 at.% Ga homogenized specimen that was thermal-cycled between -195 and 25°C shown in Fig. 4 lies below the line contain-

ing the data points for the pressure-induced phase mixtures. It is not far above the line connecting the data points for the δ -phase and the α' -phase. This strongly suggests that very little if any amorphous state forms during the thermally induced transformation.

The specimen that was isopressed to 10.3 kbar with a 30 min hold at pressure was subsequently held a total of 193 h between 75 and 110°C , which are high homologous temperatures for the α -phase, and produced the triangular data point in Fig. 4. The specimen is moving from a two-phase mixture of α' -phase and amorphous state toward a two-phase mixture of α' -phase and δ -phase. Thus I conclude that the amorphous state is crystallizing into the δ -phase during this low temperature heat treatment. We also know from lattice parameter measurements that the α' -phase in this specimen is becoming less expanded after this thermal treatment and thus more dense ($\sim 19.4 \text{ g}/\text{cm}^3$).

4. Effects of further thermal treatments on density and compressibility specimens

We later heated the specimen that was first isostatically pressed to 10.3 kbar (point 1 in Fig. 5) into the β -phase temperature region. The specimen was held for 16 h at 140°C , cooled to RT, and the density and compressibility measured. This is shown as point 2 in Fig. 5. Subsequent heat treatments of 16 h each, also in the β -phase temperature region, at 160, 180, and 200°C , did not change the density or the compressibility of the specimen. After these heat treatments, the specimen was cycled 3 times between -80 and 100°C , a treatment known to convert any β -phase present to the α -phase. The density and compressibility data point after this step is shown as point 3 in Fig. 5. We now know that when we heat a Pu–1.7 at.% Ga specimen that

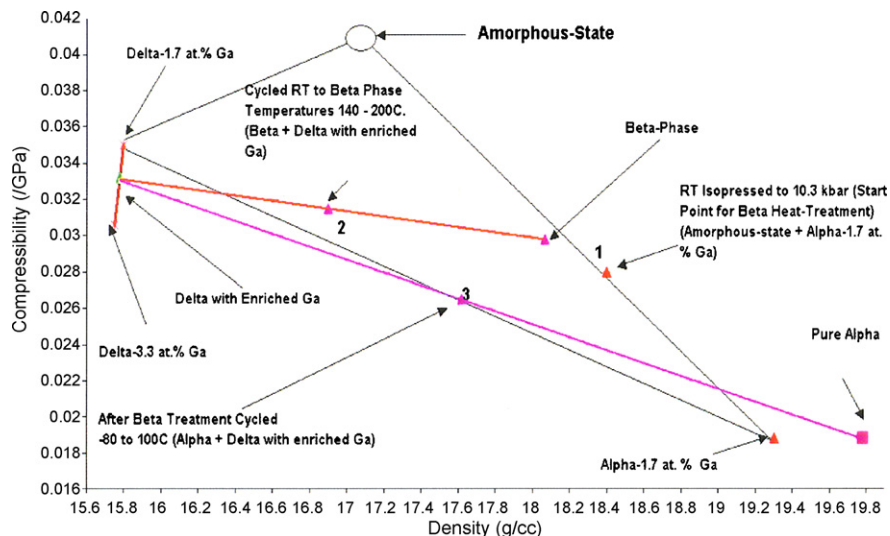


Fig. 5. Density and Compressibility data taken at RT. Starting with the Pu-1.7 at.% Ga alloy specimen hydrostatically pressed to 10.3 kbar at RT (point 1). Specimen was heat-treated a total of 16 h each at temperatures of 140, 160, 180 and 200 °C (all temperatures in the β -phase temperature region). Room temperature density and compressibility measurements after these treatments all gave the same values (point 2). After this step the phases would be Ga depleted β -phase and Ga enriched δ -phase. The next data point 3 shown on this plot is after thermal cycling the material 3 times between -80 and 100 °C, which increased the density to 17.62 g/cm³. After this step the phases would be Ga depleted α -phase and Ga enriched δ -phase. By constructing the pink line from the pure α -phase data point through this latter two-phase data point and extending it to the δ -phase, we find that the δ -phase is indeed enriched in Ga. Again constructing the orange line from this enriched δ -phase data point through point 2, we find that the compressibility of the β -phase is 0.030 GPa⁻¹.

has some pressure-induced α' -phase into the β -phase temperature region, that the α' -phase will transform to the β -phase and that most of the Ga entrapped in the α' -lattice will not be trapped in the β -lattice. The reason I conclude that there is almost no Ga in the β -lattice is based on the fact that the β -lattice parameters are not changed at this point, thus indicating that there is little or no Ga in the lattice. However if the value were zero, then the β -phase would transform to the α -phase above RT. We have also learned, that for an alloy of this composition, all of the β -phase will transform back to the α -phase after the low-temperature thermal cycles used in this experiment.

The formation of the β -phase causes the Ga, which had been entrapped in the α' -lattice, to simply move into the adjacent amorphous-state, which causes the amorphous state to crystallize into the δ -phase. The phase mixture after the β -phase heat treatment consists of Ga-depleted β -phase and Ga-enriched δ -phase. Likewise the phase mixture after the thermal cycling to -80 °C consists of Ga-depleted α -phase and the same Ga-enriched δ -phase. With only two-phases present after the thermal cycling to -80 °C, it follows that this data point should lie on the line drawn between these two phases: the α -phase and the Ga-enriched δ -phase. The pink line was constructed by connecting the α -phase data point on the right with this latter data point and extending the line to the δ -phase data point region on the left. We can see that this line intersects the line between the δ -phase data points for the 1.7 and 3.3 at.% Ga alloys. Since the intersection is about halfway between these two values, it indicates that the δ -phase is indeed enriched in Ga above the original value just as I predicted. This supports my previous conclusion that the data point after the β -phase heat treatments consists of only the Ga-depleted β -phase and the same Ga-enriched δ -phase. Since we now know the data point for this Ga-enriched δ -phase, it is possi-

ble to draw the orange-line from that data point through the two-phase data point (2) and project this line to the calculated density of the β -phase, and we see that the β -phase has a compressibility near 0.030 GPa⁻¹.

The most profound result of this analysis is the identification of the amorphous state in these isopressed specimens. It must be emphasized that we do not believe that the amorphous state is an equilibrium state, but rather it is a state that only exists under very specific conditions. One result that is surprising is that once formed, generally after complex stress states exist, the material is quite stable even at elevated temperatures where these same stress states would be greatly alleviated. There is no doubt that the development of high-dislocation densities and general disorder during the pressure transformation process leads to the initial formation of the non-periodic amorphous state. It could be speculated that the formation of the amorphous state involves an enhanced overlap of the 5f-electron orbitals into a bonding mode, which accounts for the increased density and surprising stability.

5. Incremental pressurization results on Pu-Ga alloys

In the course of trying to understand the effects of Ga content on the pressure transformation of the homogenized δ -phase alloys, Zukas and Pereyra [13] performed some incremental pressurization cycles in his pressure dilatometer. Some observations on these experimental pressure transformation curves are:

- (1) No reversion occurs upon pressure release in the Pu-1 at.% Ga alloy even after small incremental pressure cycles.

- (2) Significant reversion occurs upon pressure release in the Pu–1.7 and Pu–2.5 at.% Ga alloys after small incremental pressure cycles.
- (3) After 7 kbar no reversion occurs, upon pressure release, in the Pu–1.7 at.% Ga alloy.
- (4) After 10 kbar almost no reversion occurs, upon pressure release, in the Pu–2.5 at.% Ga alloy.

We already know that once the two lower Ga content alloys reach 10 kbar that they consist of only two phases: α' -phase and amorphous state (Fig. 3). We can easily calculate the densities of the dilatometric specimens as a function of pressure. If in the course of the transformation there are only two phases, then the amounts of each phase at any given pressure can be calculated from these densities. If we have three phases present during a transformation, the quantities of each phase can only be calculated from the mixture density if the quantity of one of the phases is known. By calculating the amount of the phases present where only two phases exist and assuming that the transformation of the δ -phase forms a smooth curve as a function of pressure it is possible to calculate the transformation mixtures as a function of pressure. From these calculations some interesting trends are evident. In the lowest Ga content alloy which forms large quantities of the amorphous-state early in the transformation process no reversion of the transformation is evident even after small incremental pressure cycles. In the highest Ga content alloy the amorphous state only begins to form near the maximum pressure of 10 kbar and it is only after the amorphous state begins to form that the transformation does not revert upon pressure release. From my calculations it appears that once about 20% amorphous state forms the reverse transformation no longer occurs upon pressure release. Since the initial $\delta \rightarrow \alpha'$ transformation is martensitic [14], and requires crystallographic alignment between the two phases, the reverse transformation can only occur as long as that crystallographic alignment is preserved. I believe the introduction of the amorphous state disrupts this alignment and thus makes the reverse transformation inoperative.

6. High pressure phase identification

Akella and Smith [15] performed diamond anvil cell experiments with a 2.1 at.% Ga homogenized δ -phase alloy. As he pressurized the δ -phase alloy he reported that he began to see the α -phase diffraction lines growing at the expense of the δ -phase diffraction lines until he reached a pressure of about 7–8 kbar, at which point all he could detect was the α -phase; the δ -phase had completely disappeared. Pressure dilatometry on the other hand indicates that a specimen of this alloy content is less than half α -phase at a pressure of 8 kbar. While it is inarguable that X-ray diffraction measurements are much more difficult in a diamond cell experiment than for normal X-ray diffraction measurements, the fact is still true that the δ -phase is much easier to detect than any of the other phases of Pu. These results certainly are in consort with our conclusions that significant amounts of the amorphous-state forms in these pressure-transformed Pu–Ga alloys.

7. Response of α' -phase and amorphous state to temperature

We have already examined the work of Zukas on his pressure dilatometric work. From my analysis I concluded that after a 10 kbar pressure cycle the three Pu–Ga alloys we examined have the following phase mixtures:

- Pu–1.0 at.% Ga – 87% α' -phase + 0% δ -phase + 13% amorphous-state,
- Pu–1.7 at.% Ga – 66% α' -phase + 0% δ -phase + 34% amorphous-state, and
- Pu–2.5 at.% Ga – 68% α' -phase + 12% δ -phase + 20% amorphous-state.

The response of these three alloys to a heating cycle after the above treatment is quite different. In the heating curve for the 2.5 at.% Ga alloy, there is both a slow transformation taking place throughout the heating cycle and a more rapid $\alpha' \rightarrow \delta$ transformation just below the normal $\alpha \rightarrow \beta$ transformation temperature. Even though the 20% amorphous state in this specimen was enough to disrupt the $\alpha' \rightarrow \delta$ transformation on pressure release, there obviously is not enough to prevent the transformation during the heating cycle. Since the amorphous state is continuously crystallizing back to the δ -phase throughout the heating cycle, this may encourage the reverse transformation on heating because of lowering the amount of the amorphous state. It is interesting that above the normal $\alpha \rightarrow \beta$ transformation temperature that some amorphous state is still crystallizing into the less dense δ -phase. This shows that without the micro-segregation of Ga that occurs during an $\alpha' \rightarrow \beta$ transformation that some amorphous state can exist up to 200 °C, even in this high Ga content alloy.

For the two lower Ga content alloys, there are very large $\alpha' \rightarrow \beta$ transformations near the normal $\alpha \rightarrow \beta$ transformation temperature. In simply looking at the differences in the length changes between RT and 140 °C it is obvious that the Pu 1.7 at.% Ga alloy has, in addition to the $\alpha' \rightarrow \beta$ transformation, undergone a large density change from the crystallization of the amorphous state and the $\alpha' \rightarrow \delta$ transformation. The amorphous state in the Pu–1.7 at.% Ga alloy begins crystallizing into the δ -phase near RT, but this crystallization is complete concurrent with the $\alpha' \rightarrow \beta$ transformation. The reason that the amorphous-state completely crystallizes to the δ -phase in this latter alloy concurrent with the $\alpha' \rightarrow \beta$ transformation is believed to be due to the movement of Ga into the amorphous state from the β -phase as it forms.

8. The effect of stress on the δ -phase

Eash and Hecker [16] reported that the Pu–1.7 at.% Ga homogenized δ -phase alloy easily transforms to the α' -phase under hydrostatic compression. They reasoned that the transformation was displacive-diffusionless and therefore both the shear and normal stresses should be expected to influence the transformation. In subjecting a Pu–1.7 at.% Ga specimen to uniaxial compression, they found that the δ -phase did not transform

even when loaded to a strain level of 1.51. They subjected δ -phase specimens to very large strain levels in shear and did not achieve any transformation. Hecker and Eash concluded that for the Pu–1.7 at.% Ga alloy, the hydrostatic stress component plays the major role in governing the stress-assisted transformation.

Unlike most martensitic transformations that are displacive-diffusionless and involve a transformation from one crystalline form to another, the δ -phase of plutonium transforms into a mixture of a crystalline form (the α' -phase) and an amorphous state. This may well be the reason that only the hydrostatic stress component is able to assist the collapse of the δ -phase into these denser states. The formation of an amorphous state is not dependant upon crystallographic planes or crystallographic alignment with the parent phase, which is required for most martensitic type transformations but is governed by pure hydrostatic pressure since it is by definition a non-crystalline disordered state.

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