LLNL-CONF-400006

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Isothermal Martensitic and Pressure-Induced (delta) to (alpha)' Phase Transformations in a Pu-Ga Alloy

A. J. Schwartz, M. A. Wall, D. L. Farber, K. T. Moore, K. J. M. Blobaum

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January 3, 2008 through January 8, 2008

Lawrence Livermore National Laboratory

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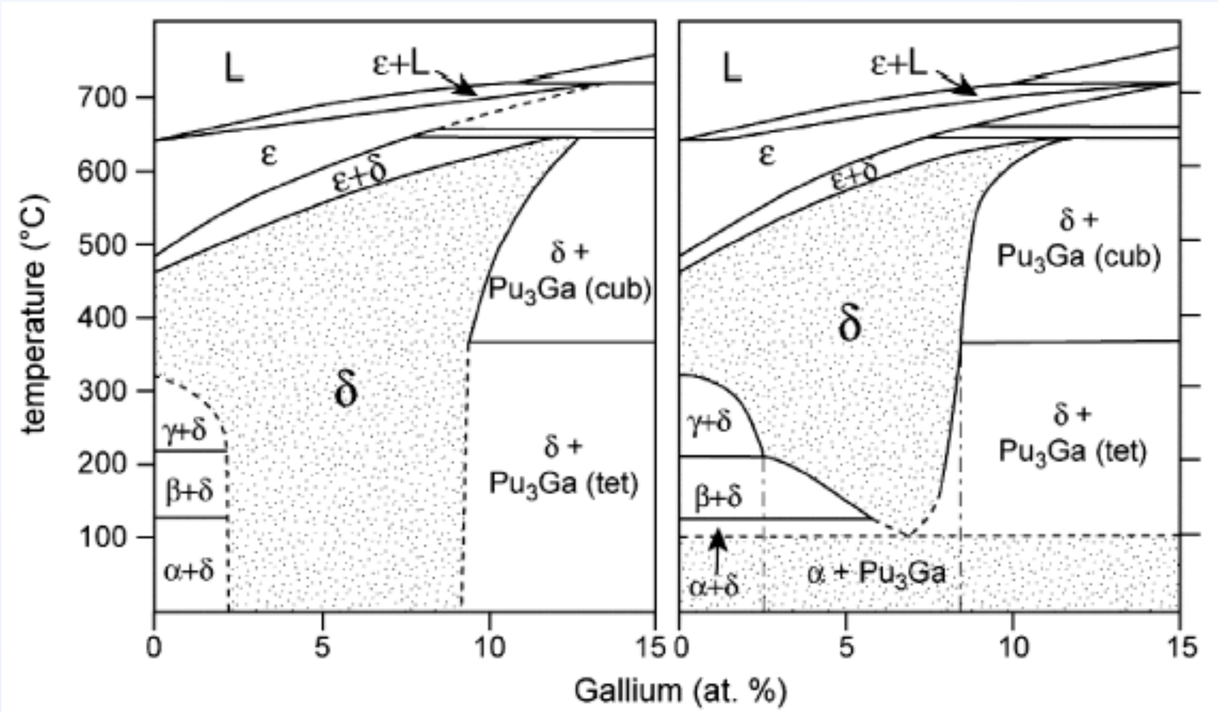
Understanding the phase transformations remains as one of the significant Pu metallurgical challenges

- Equilibrium phase diagram
- 5 allotropic phase transformations
- Effects of alloying on phase stability and properties
- Phase transformations and phase stability
  - The $\delta \rightarrow \alpha'$ isothermal martensitic transformation
    - Mechanism or mechanisms
    - Double-C curve kinetics
  - The $\delta \rightarrow \alpha'$ transformation under pressure
    - Pu-Al
    - Pu-Ga
    - Amorphous phase?
    - Characterization of the recovered sample

For decades, the "West" accepted that the δ phase was thermodynamically stable at ambient conditions

US Diagram **Russian Diagram**



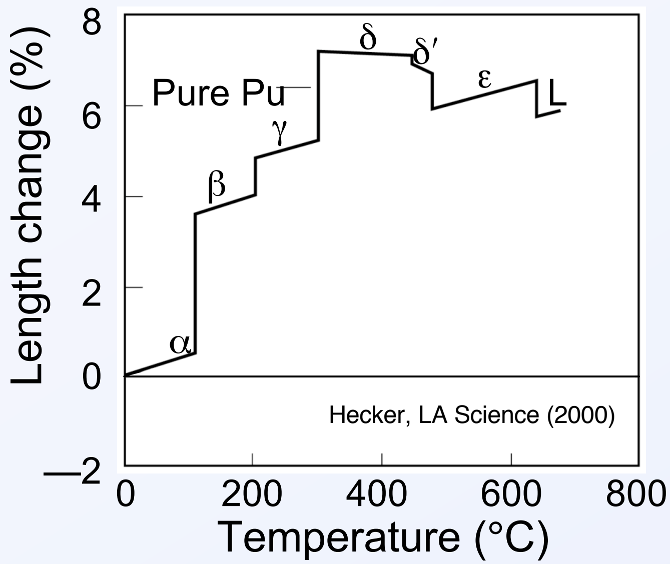
Ellinger, Land, and Struebing, J. Nuc. Mat. (1964)

Hecker and Timofeeva, LA Science (2000)

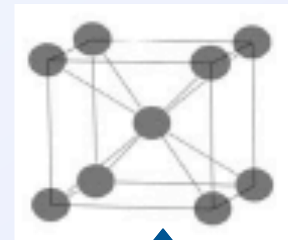
The δ-phase retained to room temperature is metastable
Timofeeva (2003) estimated 10,000 years to decompose

Chebotarev, Plutonium and Other Actinides 1975 (1975)
Adler, Met Trans (1991)
Timofeeva, Aging Studies and Lifetime Extension of Materials (2003)

Plutonium undergoes five solid-solid allotropic phase transformations between the ground state and the liquid

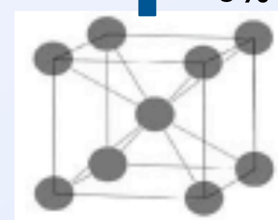


Liquid (640°C +)
ρ = 16.5 g/cm^3



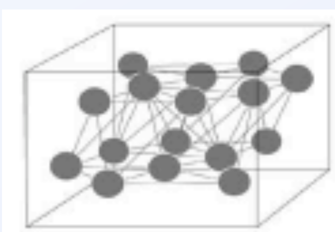
ε (486°C - 640°C)
b.c. cubic ($Im\bar{3}m$)
ρ = 16.5 g/cm^3

–3%



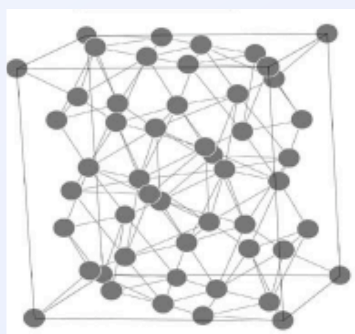
δ′ (468°C - 486°C)
b.c. tetragonal (I4/mmm)
ρ = 16.0 g/cm^3

–0.5%



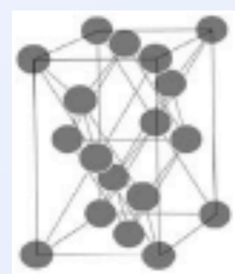
α (Low temperature - 126°C)
monoclinic ($P2_1/m$)
ρ = 19.8 g/cm^3

10%



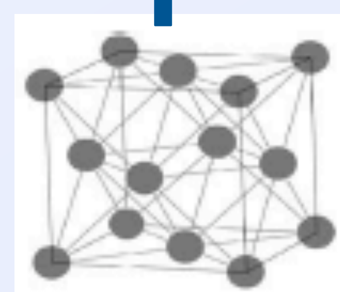
β (126°C - 214°C)
base.c. monoclinic (C2/m)
ρ = 17.8 g/cm^3

3.5%



γ (214°C - 323°C)
f.c. orthorhombic (Fddd)
ρ = 17.1 g/cm^3

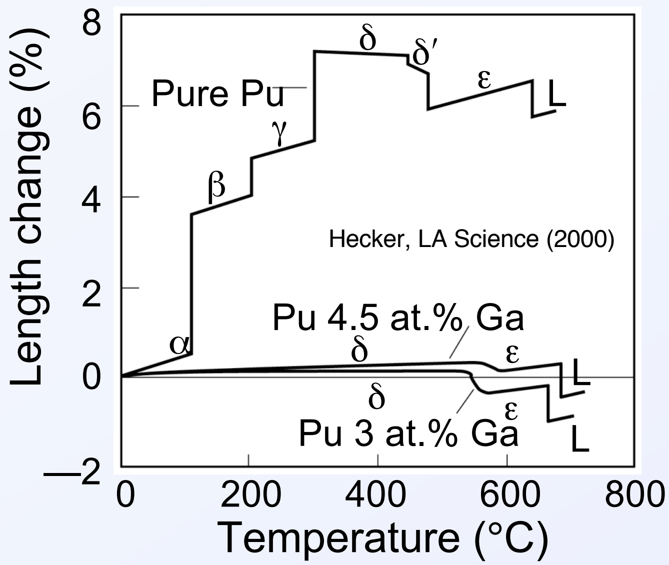
7%



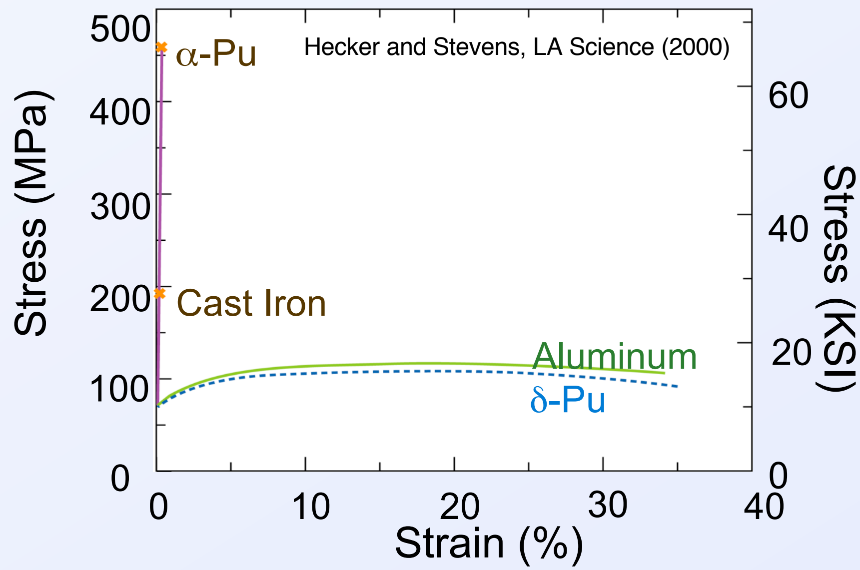
δ (323°C - 468°C)
f.c. cubic ($Fm\bar{3}m$)
ρ = 15.9 g/cm^3

Alloying plutonium with Ga retains the fcc δ-phase, reduces volume change, and improves ductility

Dilatometry of unalloyed and alloyed Pu



Tensile properties of selected materials

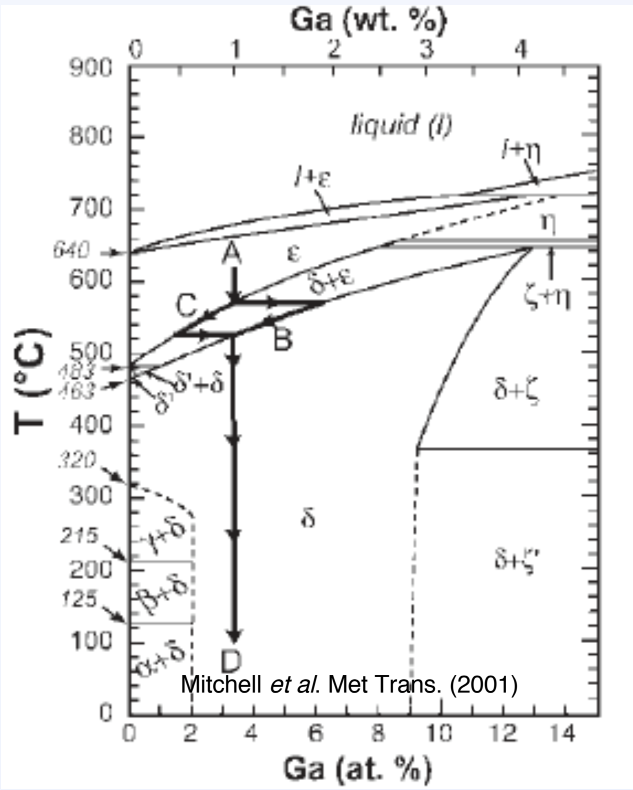


A few atomic percent Ga make plutonium easier to cast and to shape

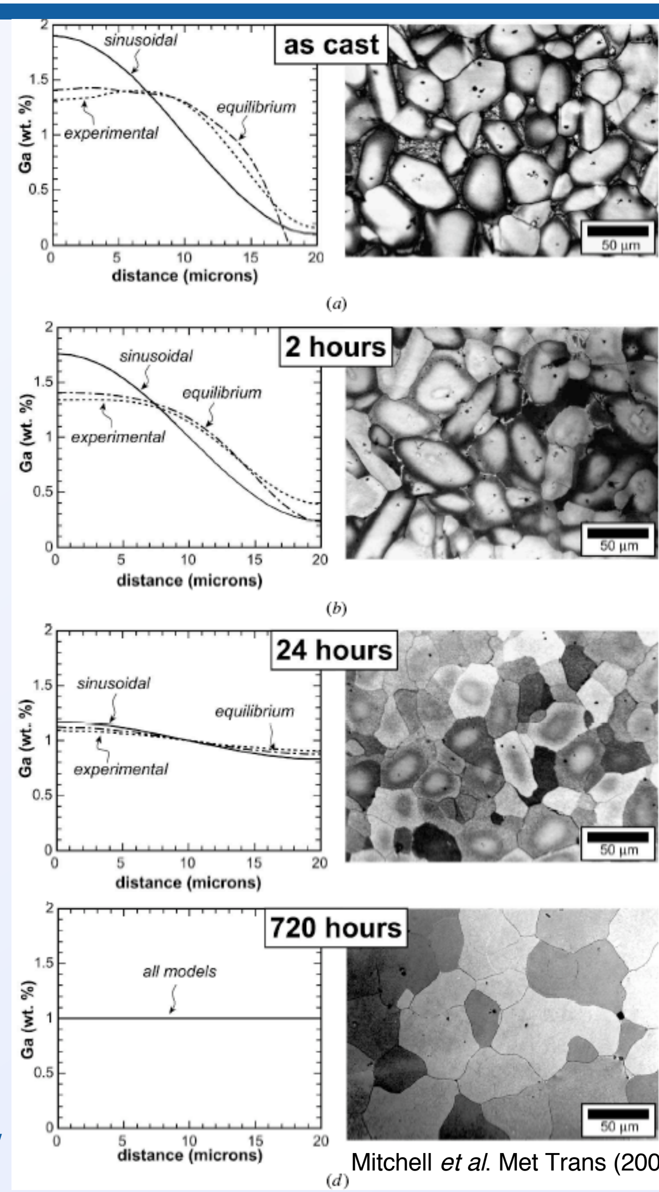
Effect of alloying

Retention of the δ-phase is dependent on the composition, cooling rate, and homogenization treatment

Pu - 1 wt.% (3.3 at.%) Ga



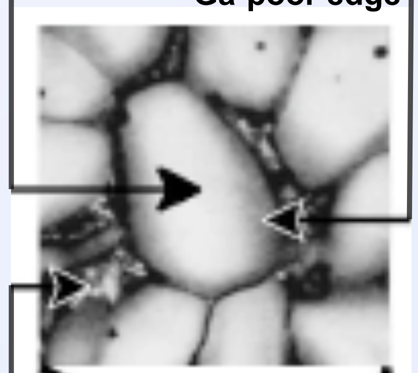
Mitchell *et al.* Met Trans. (2001)



Mitchell *et al.* Met Trans (2001)

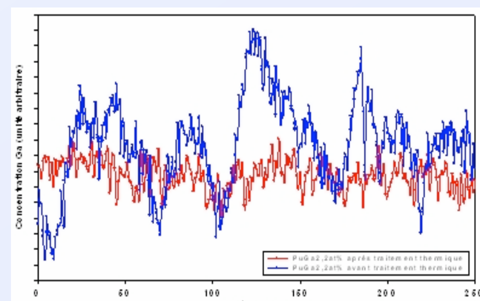
Ga-rich core

Ga-poor edge



Mitchell *et al.* Met Trans. (2001)

Intergranular α Pu

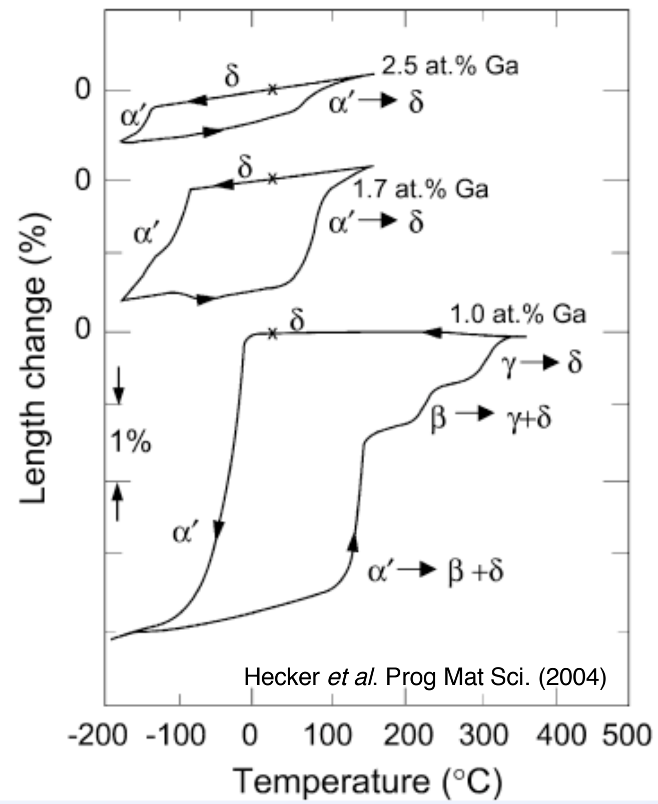


Ga distribution

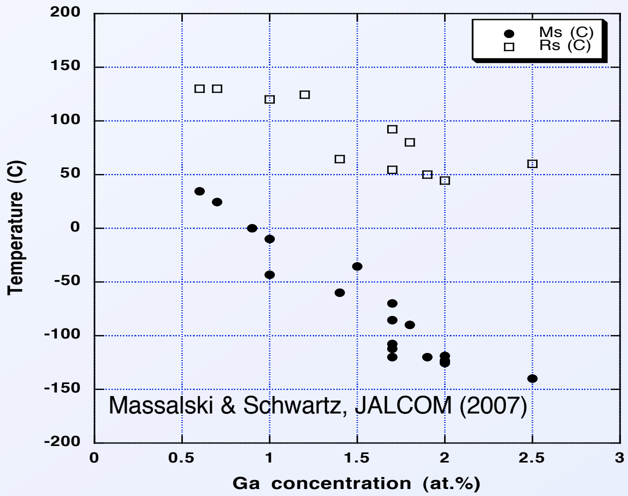
Before homogenization
After homogenization

Oudot, Ph.D. Thesis (2005)

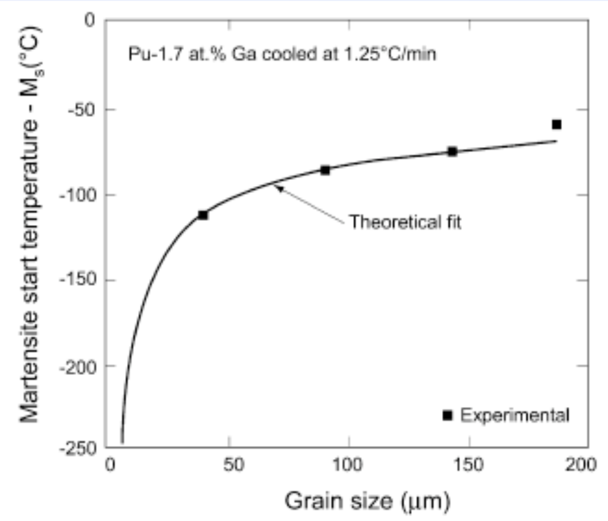
Upon cooling to sub-ambient temperatures, δ transforms to α′ via an isothermal martensitic transformation



Hecker *et al*. Prog Mat Sci. (2004)



Massalski & Schwartz, JALCOM (2007)



Adler *et al*. Met Trans. (1988)

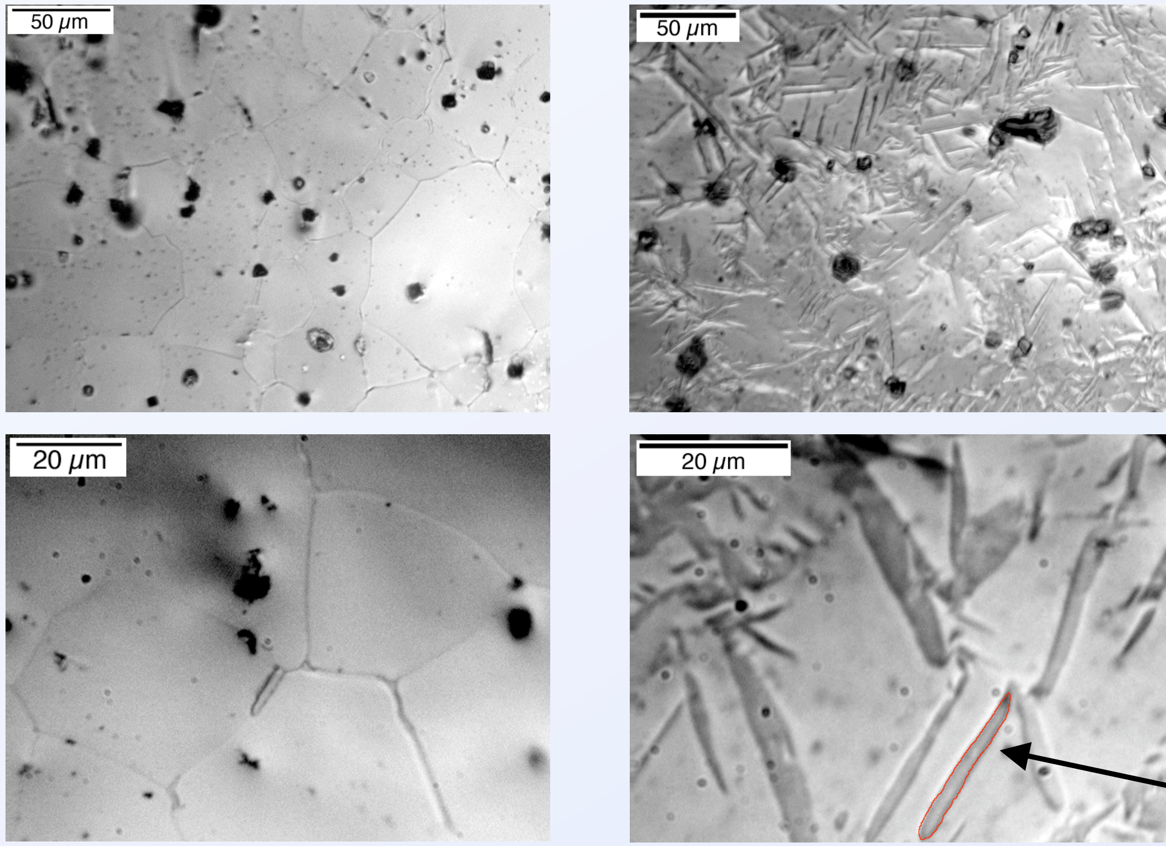
Similar to δ-phase at room temperature, α′ is also metastable

The α′ particles that form from the isothermal martensitic transformation appear as lathes in optical microscopy

Pu - 2.0 at.% Ga

440°C/12 hours | **-120°C/10 hours**

Untransformed (δ phase)



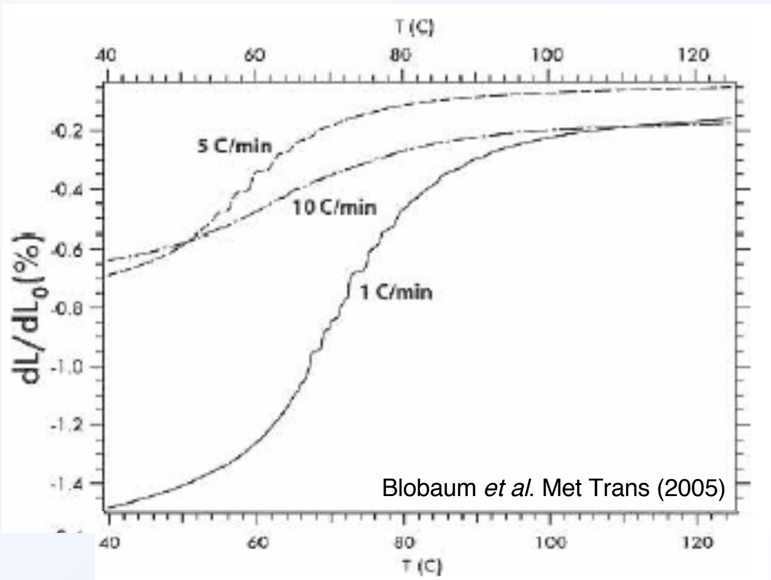
Partially transformed (δ + α' phases)

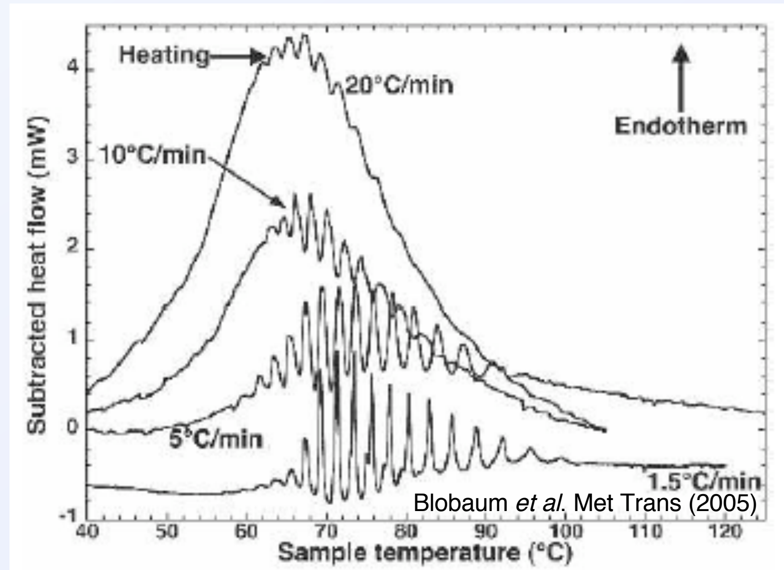
α' particle

The δ → α′ isothermal martensitic transformation goes to ~ 25% completion

α′ → δ reversion has been shown to occur via a burst martensitic mode

Pu - 2.0 at.% Ga





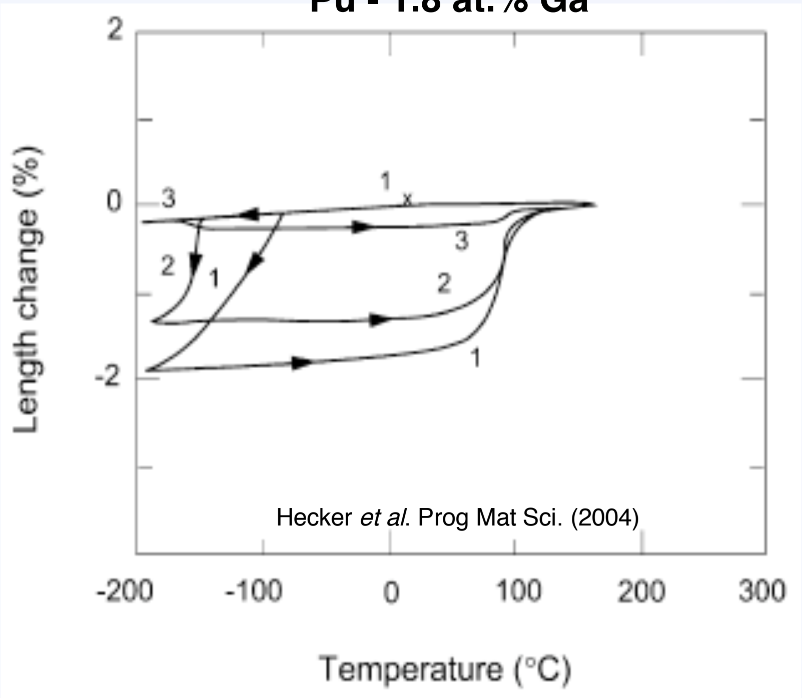
Dilatometry traces through the α′ → δ reversion exhibit steps
The derivative (dL/dt) reveals periodic spikes

Differential scanning calorimetry of the α′ → δ reversion shows periodic spikes

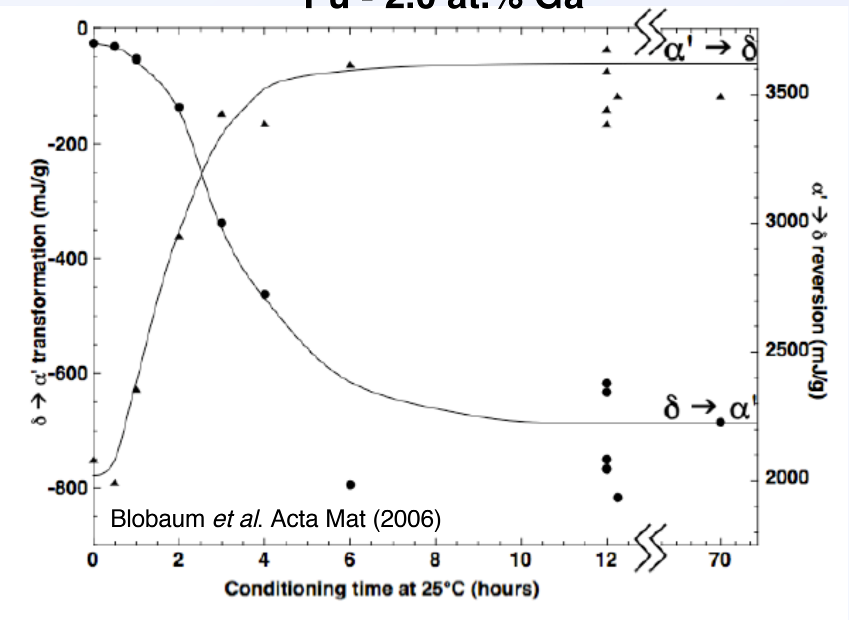
The δ → α′ isothermal martensitic transformation requires nucleation of a new phase, the reverse α′ → δ transformation does not

The amount of the $\delta \rightarrow \alpha'$ transformation is dependent on details of the thermal cycling

Pu - 1.8 at.% Ga



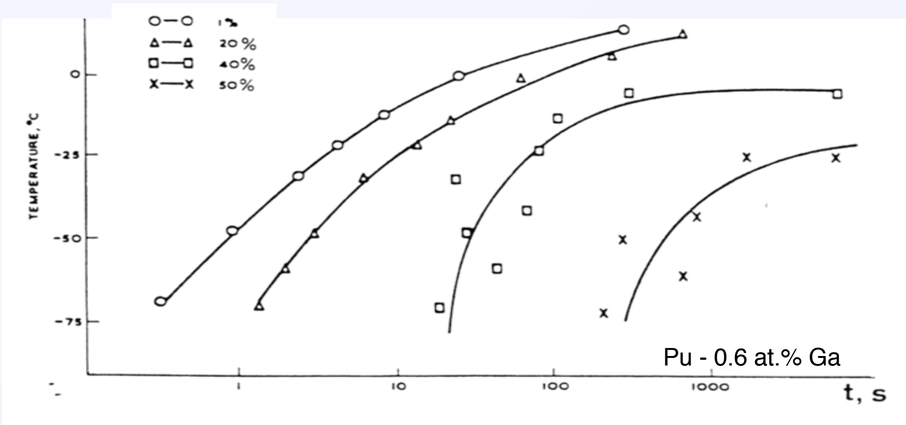
Pu - 2.0 at.% Ga

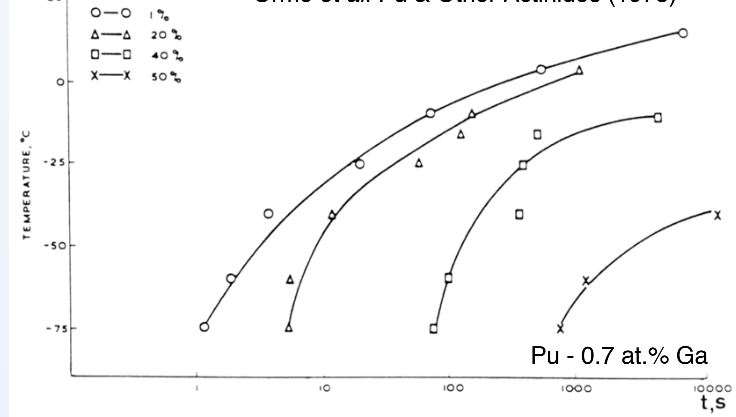


- The amount of transformation in Pu - 1.8 at.% Ga alloys decreases with each thermal cycle

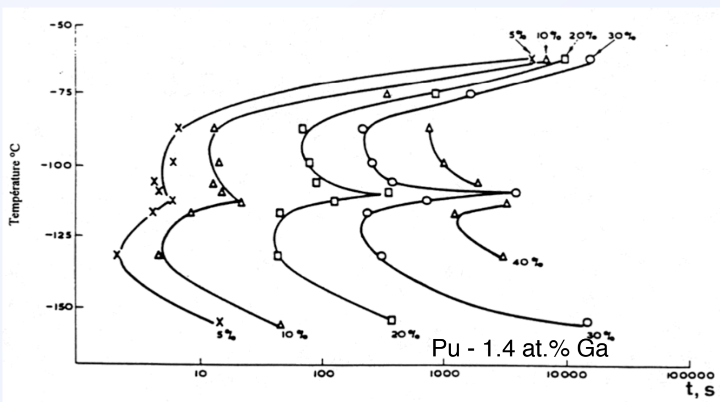
- Conditioning times of ~6 hours are required for reproducible amounts of transformation
- α_m embryos may be forming as a precursor to the $\delta \rightarrow \alpha + Pu_3Ga$
- These α_m embryos initiate α' on subsequent cooling

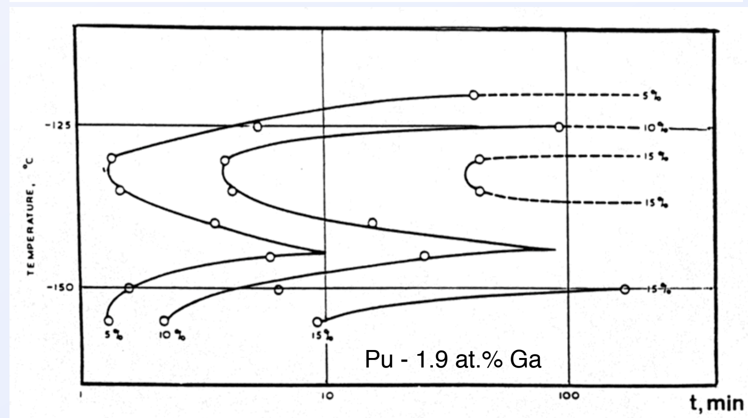
Orme *et al.* experimentally determined the kinetics of the δ → α′ isothermal martensitic transformation





Orme *et al.* Pu & Other Actinides (1975)

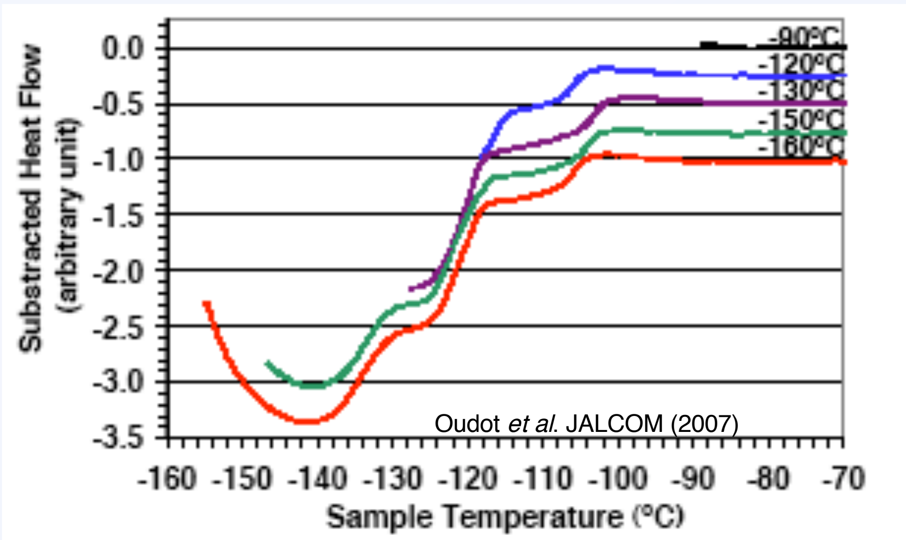


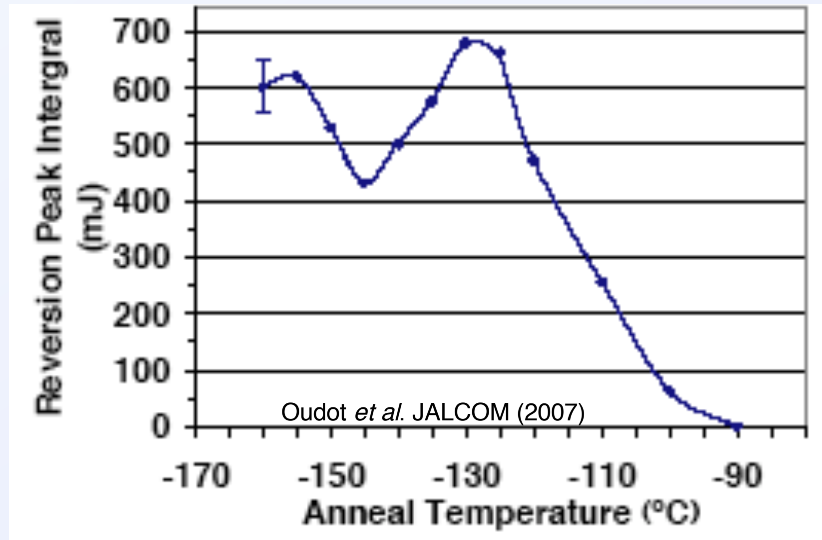


TTT diagrams of Pu-1.4 & 1.9 at.% Ga alloys show two separate knees

This behavior implies two distinct, thermally activated mechanisms must exist for this transformation

Recent DSC work by Oudot *et al*. confirms the double-C behavior and reveals interesting precursor phenomena



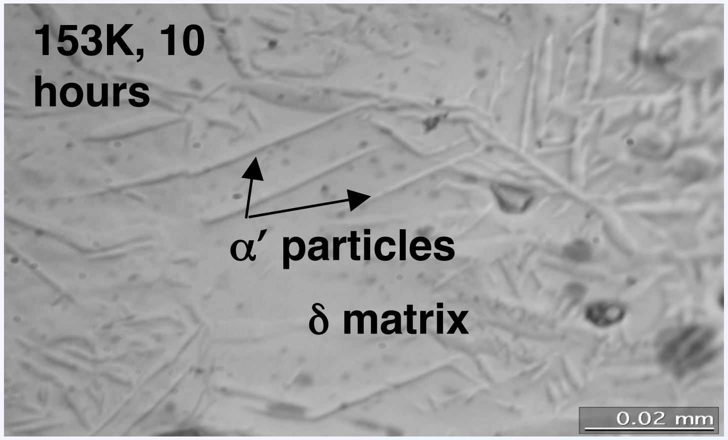


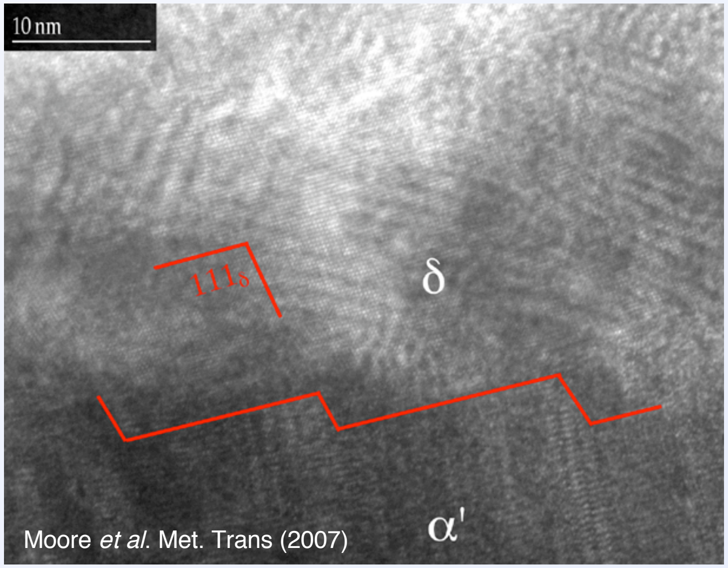
DSC scans on cooling to isothermal hold temperature reveal three peaks

The reversion peak integral (amount of $\delta \rightarrow \alpha'$ reversion) reveals two maxima after 18-hours holds

We still do not understand the origin of the double-C behavior !

The crystallography of the low-temperature δ → α′ transformation has been characterized with TEM



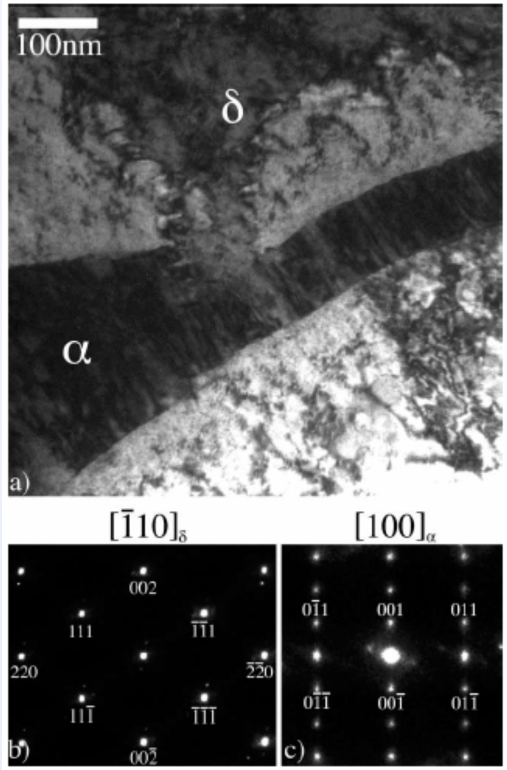


Moore *et al.* Met. Trans (2007)

- The orientation relationship between α' and δ is:
  $(111)_\delta \,||\, (020)_{\alpha'}$
  $[-110]_\delta \,||\, [100]_{\alpha'}$

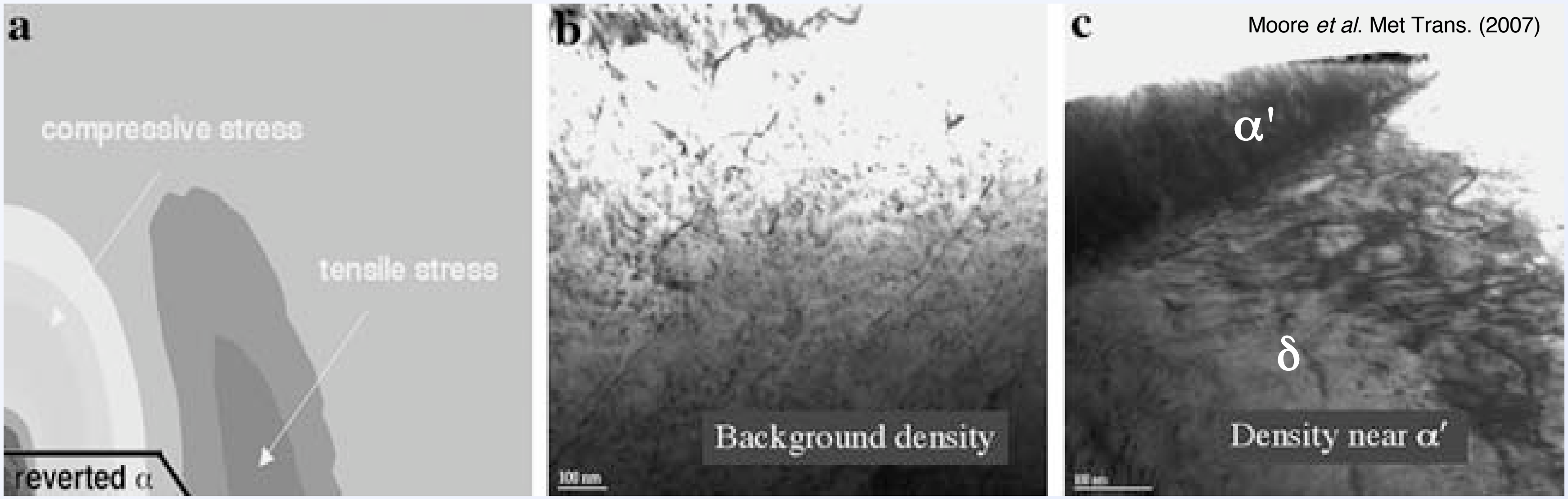
Zocco *et al.* Acta Met. (1990)

- α′ particles consist of 2 variants rotated 60° around $<020>_{\alpha'}$
- TEM shows $(205)_{\alpha'}$ twinning as a lattice invariant deformation mode
- The α'– δ interface is composed of a terrace and ledge structure that is faceted on 111_δ



Moore *et al.* Met. Trans (2007)

The large volume difference between δ and α′ is accommodated by dislocation formation and migration



Moore *et al.* Met Trans. (2007)

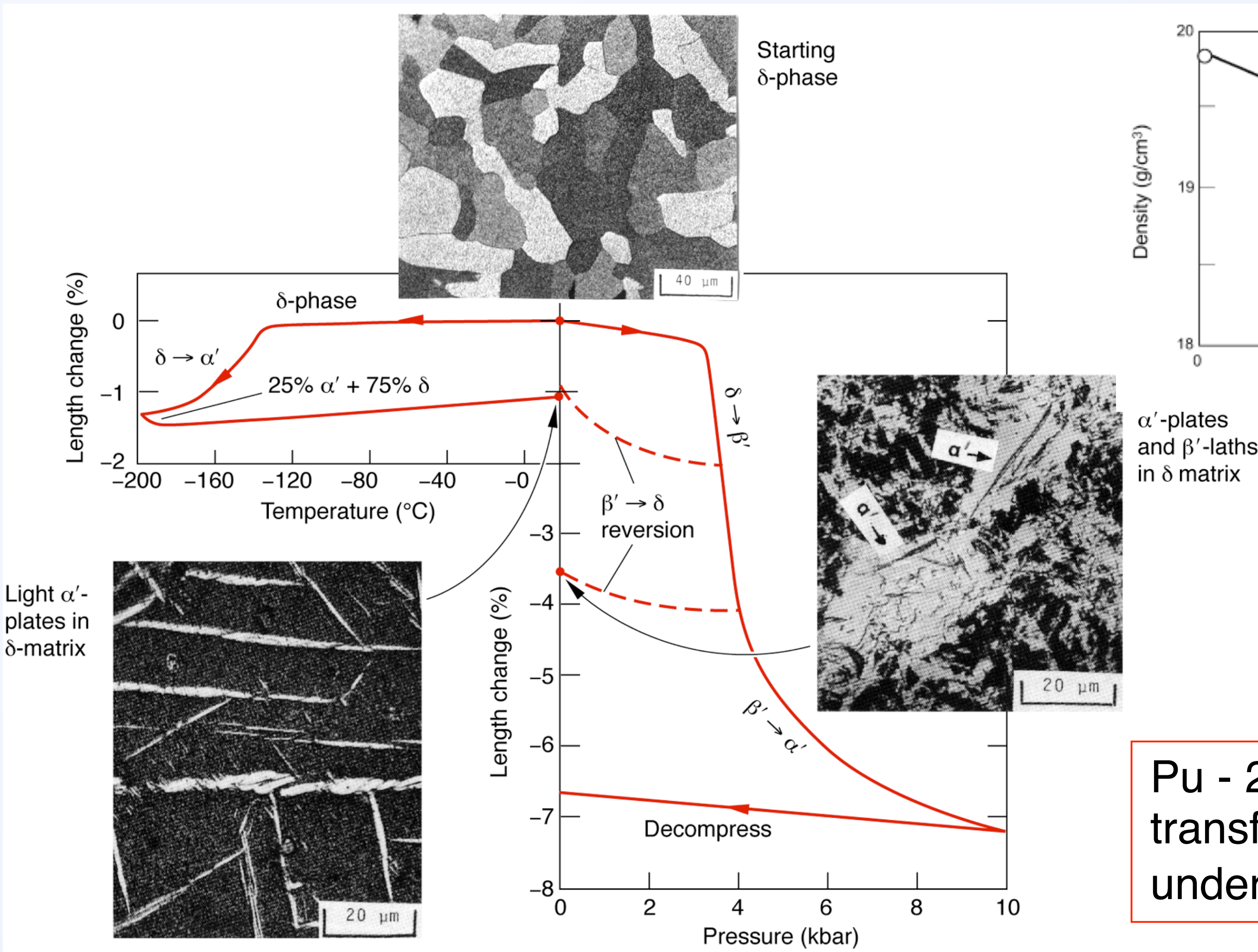
Elastic-plastic FEM analysis reveals regions of compression and tension during reversion

Background dislocation density ~ 2.2 x 10^{10} /cm^2

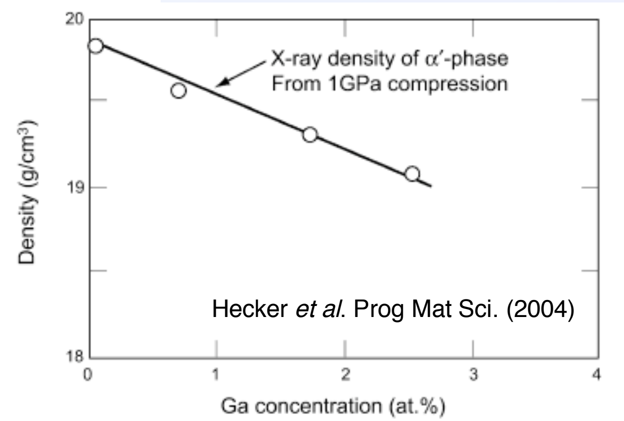
Increased dislocation density at tip of α′ particle ~ 1.7 x 10^{11} /cm^2

The dislocation density increases in the vicinity of α′ particles

The δ → α′ transformation can also be induced by pressure



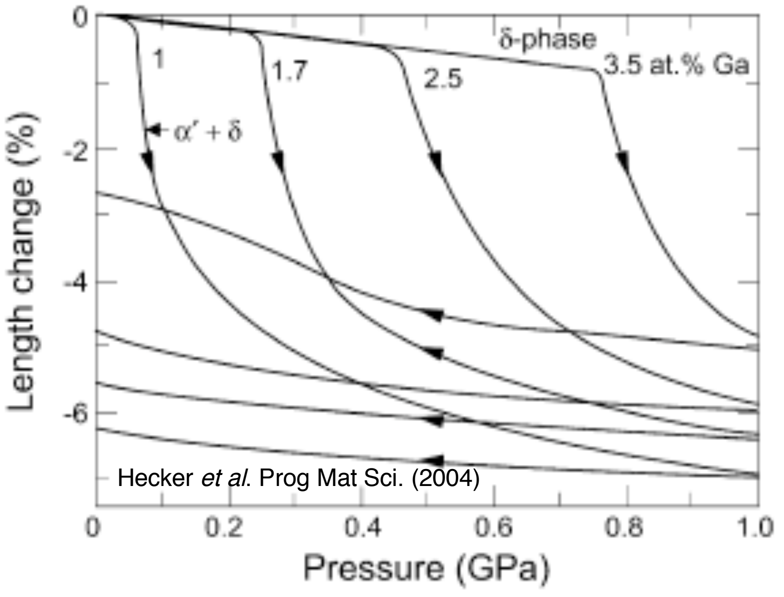
Hecker, MRS Bulletin (2001)

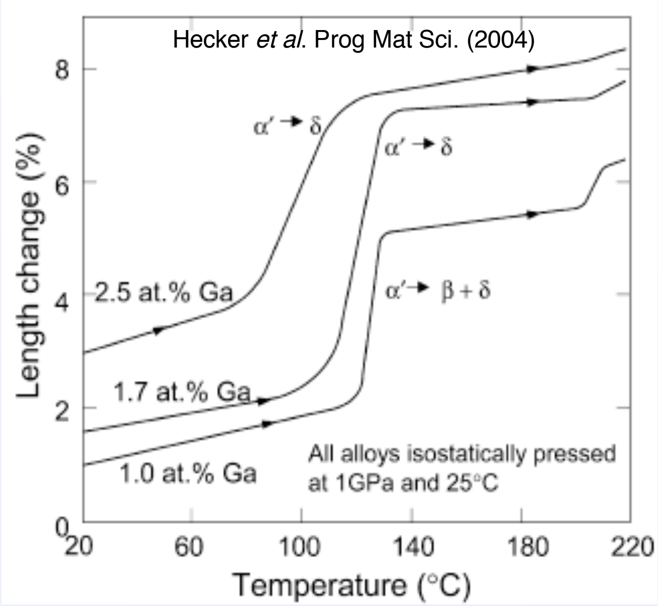


Densities of homogenized Pu-Ga alloys after isostatic pressing to 1 GPa

Pu - 2 at.% Al alloys transform first to β′ then to α′ under pressure

The δ → α′ transformation and reversion characteristics are a strong function of composition

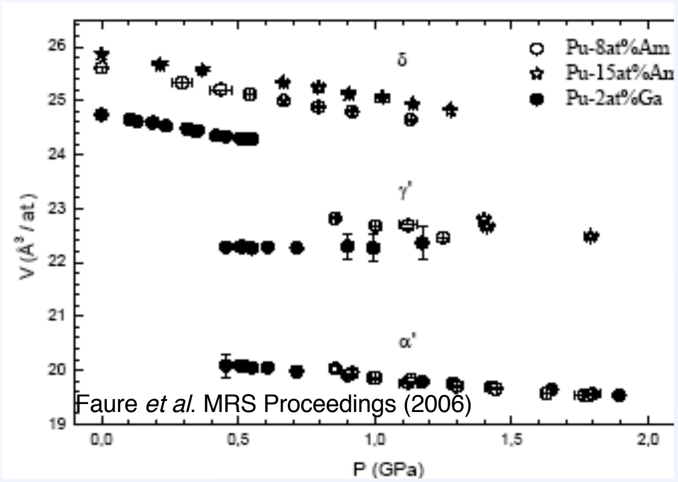




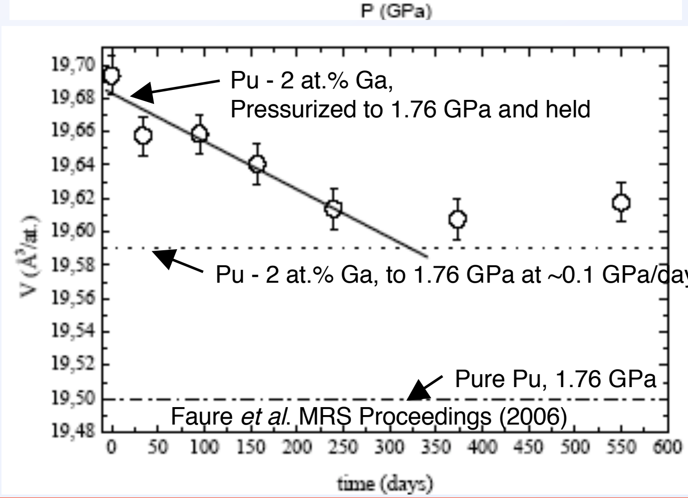
- **Under pressure, Pu - Ga alloys transform directly to α′ and undergo either a direct (α′ → δ) or indirect (α′ → β + δ → γ + δ → δ) reversion**
- **Reversion characteristics are similar to those in thermally-induced transformations**

Why do Pu-Al alloys transform through β′ whereas Pu-Ga alloys transform directly to α′? Or do they?

Diamond anvil cell experiments on a Pu - 2 at.% Ga alloy reveal δ → γ′ → α′ transformation sequence

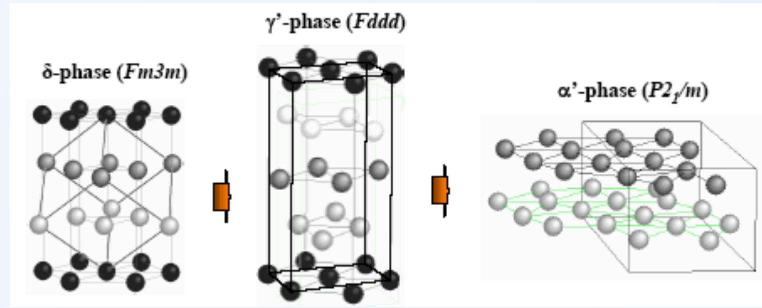


Faure *et al.* MRS Proceedings (2006)

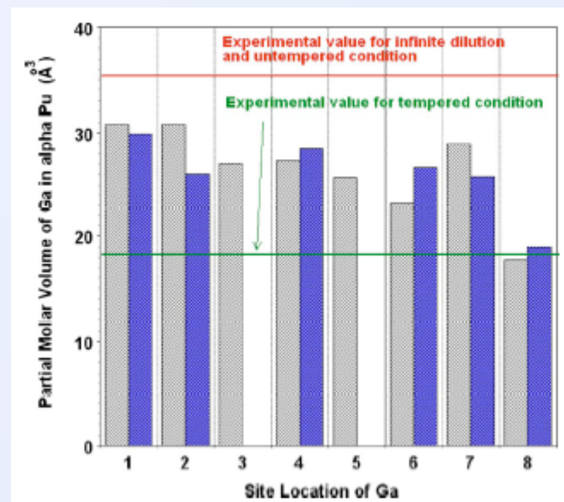


Faure *et al.* MRS Proceedings (2006)

Faure *et al.* MRS Proceedings (2006)



In the DAC, Pu - 2 at. Ga transforms through the sequence δ → γ′ → α′

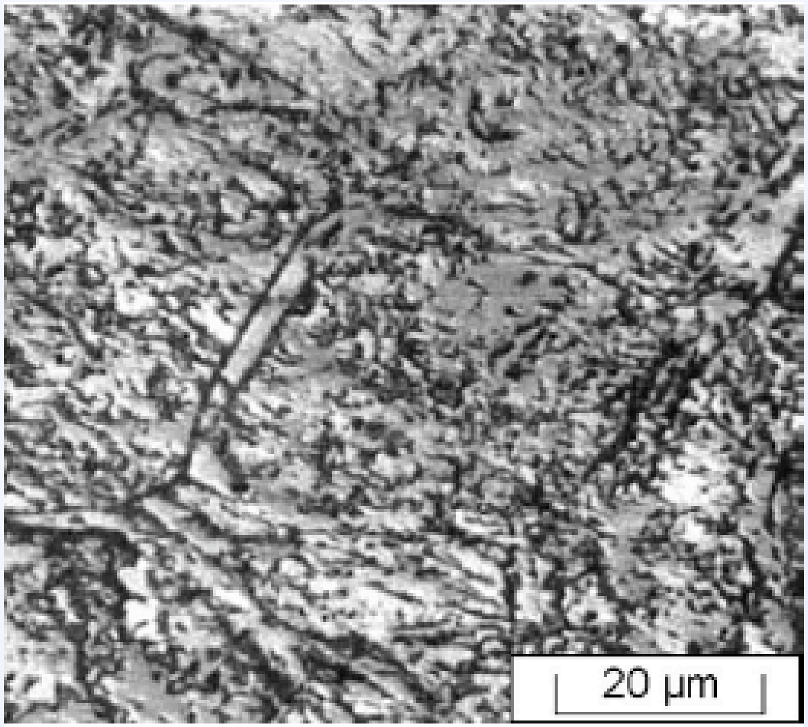


Sadigh and Wolfer, PRB (2005)

Does the time dependence of the α′ volume suggest Ga hopping to site 8?

Upon cooling, Harbur reported that a 0.68 at.% Ga alloy has a density intermediate between δ and α phases

Harbur, JALCOM (2007)



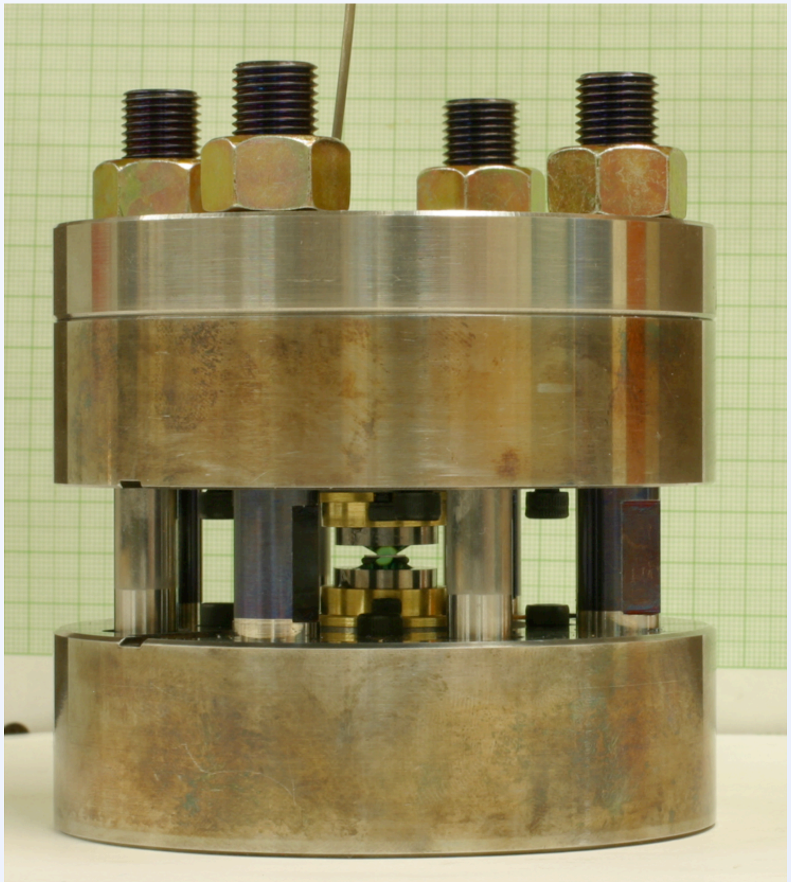
After compressing to 1 GPa

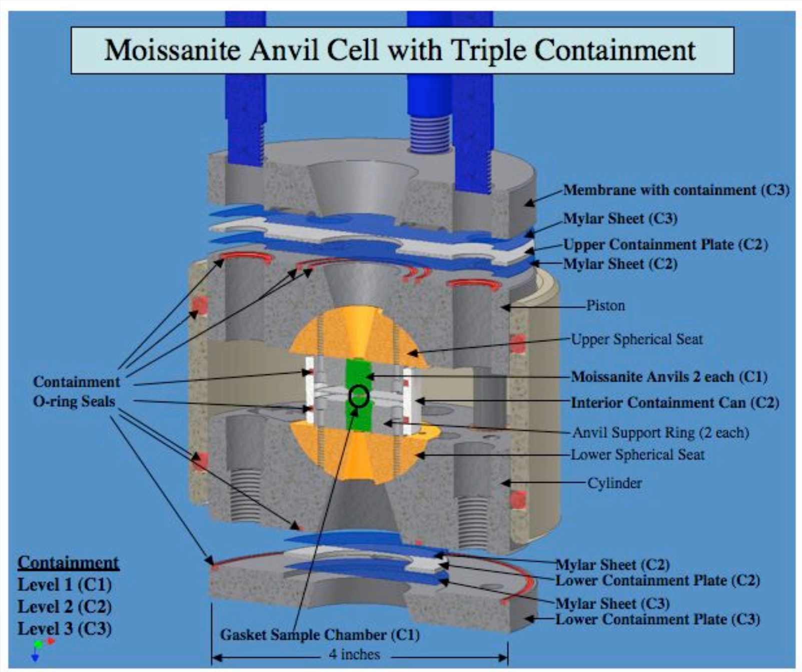
Alloy	% α′	% δ	% amorphous
1.0 at.% Ga	87	0	13
1.7 at.% Ga	66	0	34
2.5 at.% Ga	68	12	20

Harbur, JALCOM (2007)

Harbur proposes that the δ phase transforms to α′ + amorphous phase
- **on cooling low solute alloys**
- **under pressure**

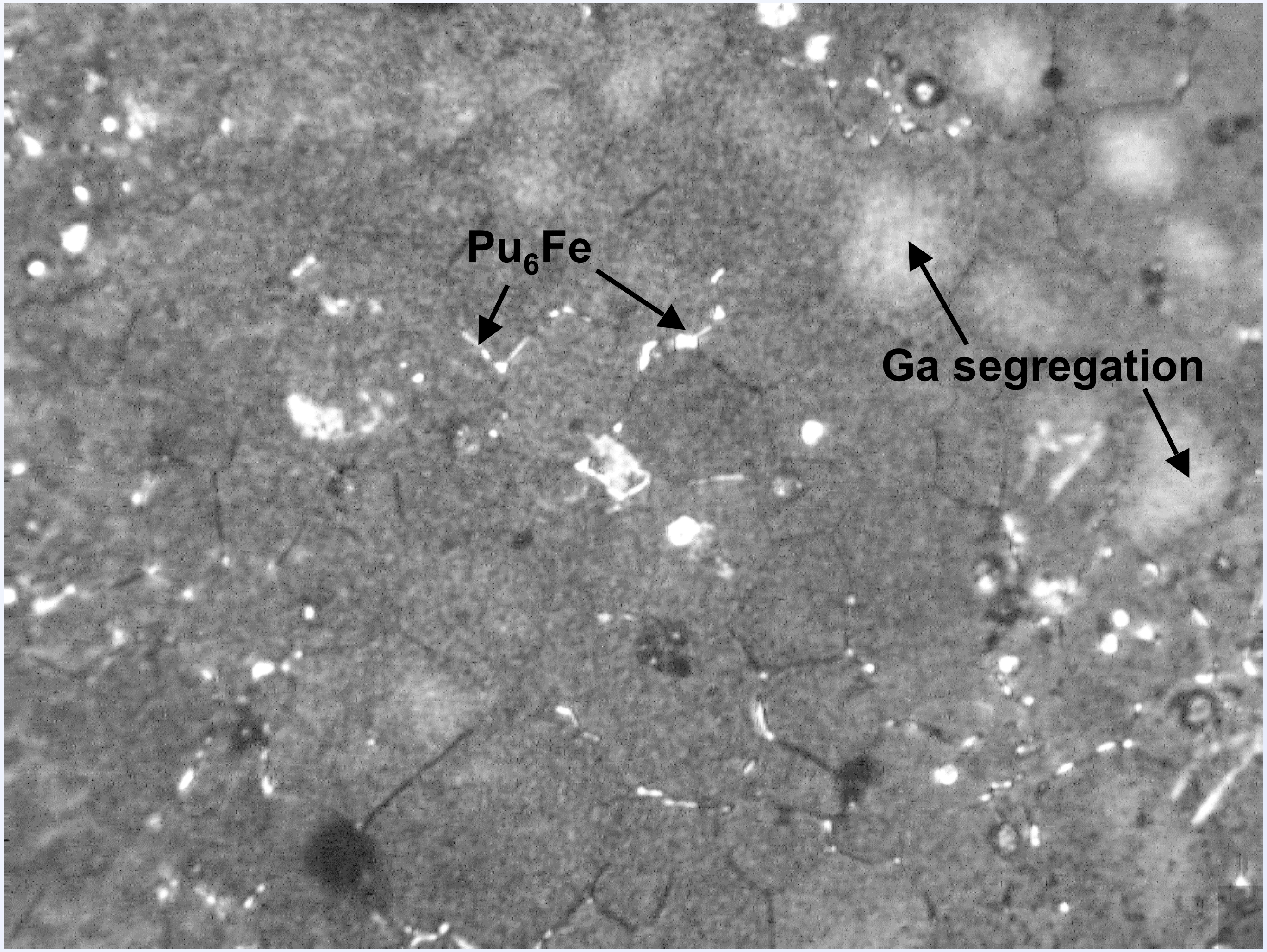
We are coupling low pressure recovery experiments with TEM to elucidate the mechanism and morphology





2.3 mm diameter specimens are slowly compressed to 1 GPa in the large volume moissanite anvil cell

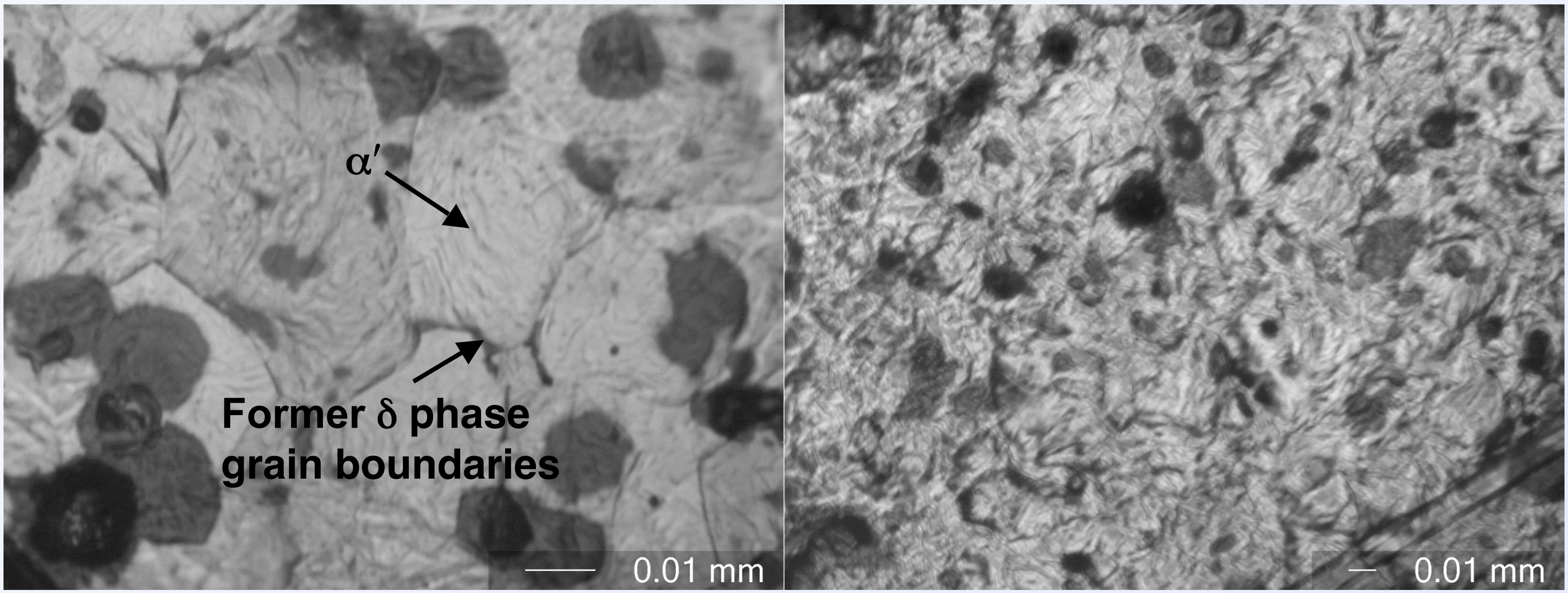
Optical microscopy of the uncompressed alloy reveals evidence of Pu_6Fe and Ga segregation



Uncompressed alloy, as received microstructure

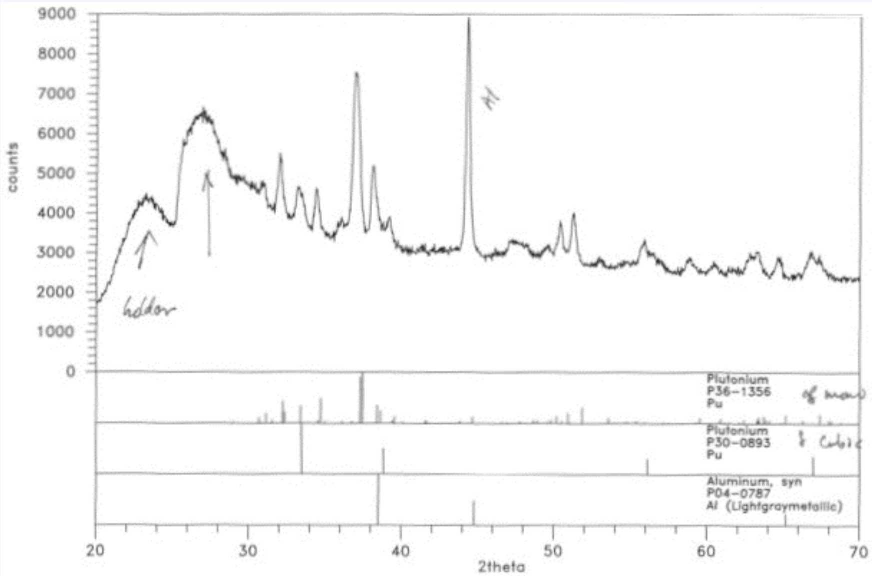
Optical microscopy of the compressed specimen reveals α′ and former δ phase grain boundaries

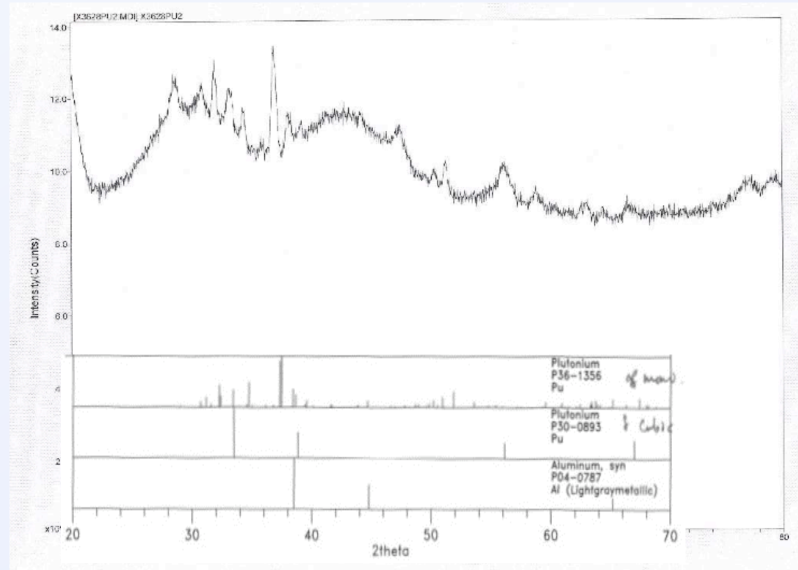
Optical microscopy images of reference alloy after hydrostatic compression



Optical microscopy does not have the resolution to differentiate between phases

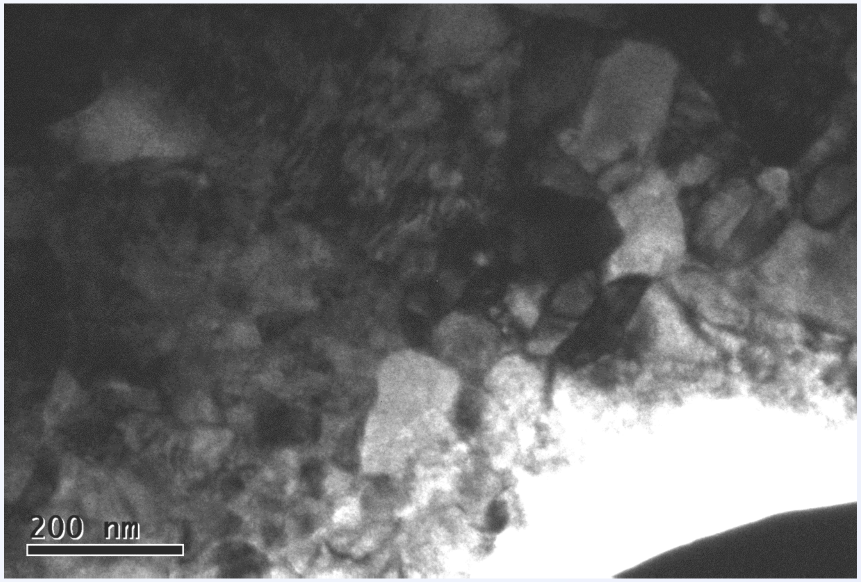
X-ray diffraction of the compressed sample reveals peaks from α′ and δ

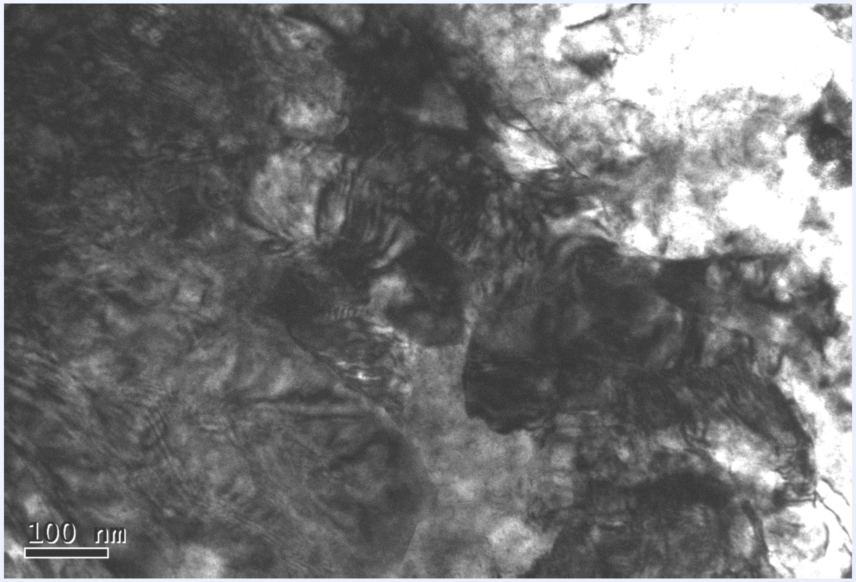




Our X-ray diffraction does not indicate the presence of an amorphous phase

Preliminary TEM reveals fine-grained α′ and small amounts of δ – no evidence of an amorphous phase

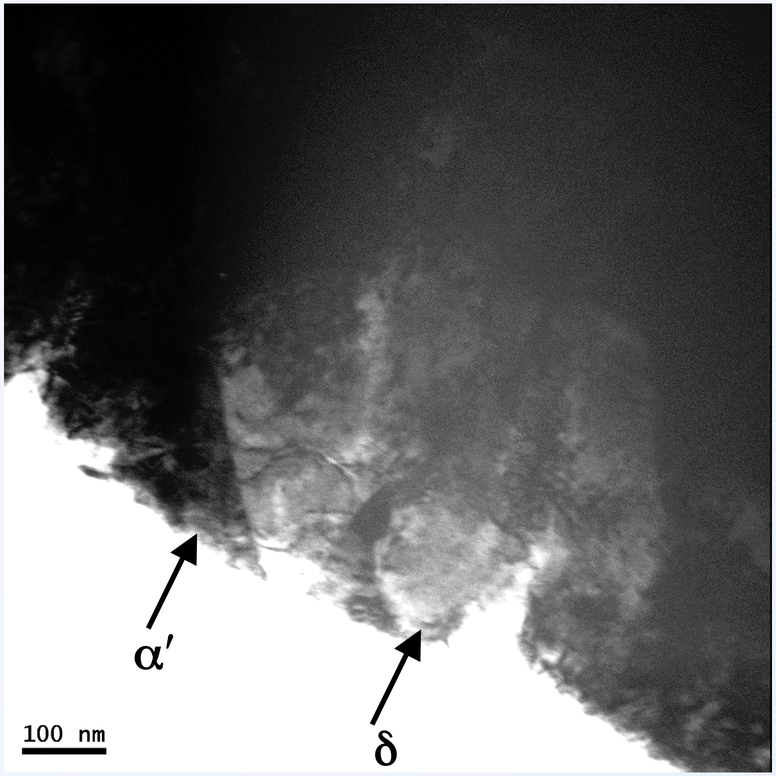


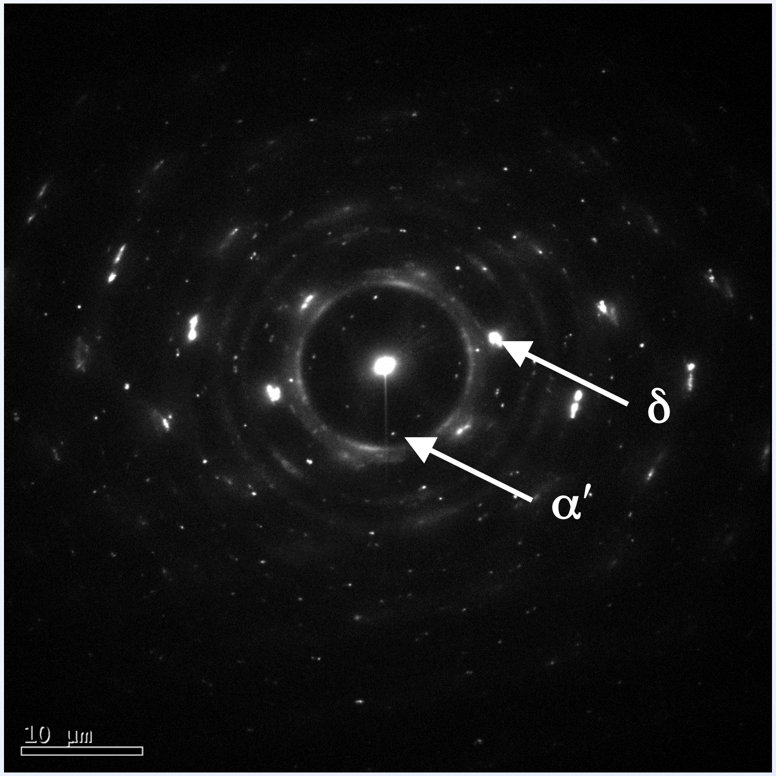


Pressure-induced δ → α′ transformation
- **Average α′ grain size ~ 100s nm**
- **Implies nucleation dominated mechanism**

Low-temperature-induced δ → α′ isothermal martensitic transformation
- **Average α′ particle size ~ 1000s x 10,000s nm**
- **Implies nucleation limited mechanism (strain)**

Preliminary TEM reveals fine-grained α′ and small amounts of δ – no evidence of an amorphous phase





δ phase is observed dispersed between the α′ grains

- High dislocation density
- No apparent orientation relationship (yet)

Summary

- Low temperature isothermal δ → α′ transformation
  - Nucleation limited
  - Lath-shaped particles
  - Intermediate phases possible
- Pressure-induced δ → α′ transformation
  - Nucleation dominated
  - Very fine grain size
  - No evidence of the amorphous phase
  - Intermediate phases likely