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Low-Temperature Martensitic and Pressure-Induced Delta to Alpha-Prime Phase Transformations in a Pu-Ga Alloy

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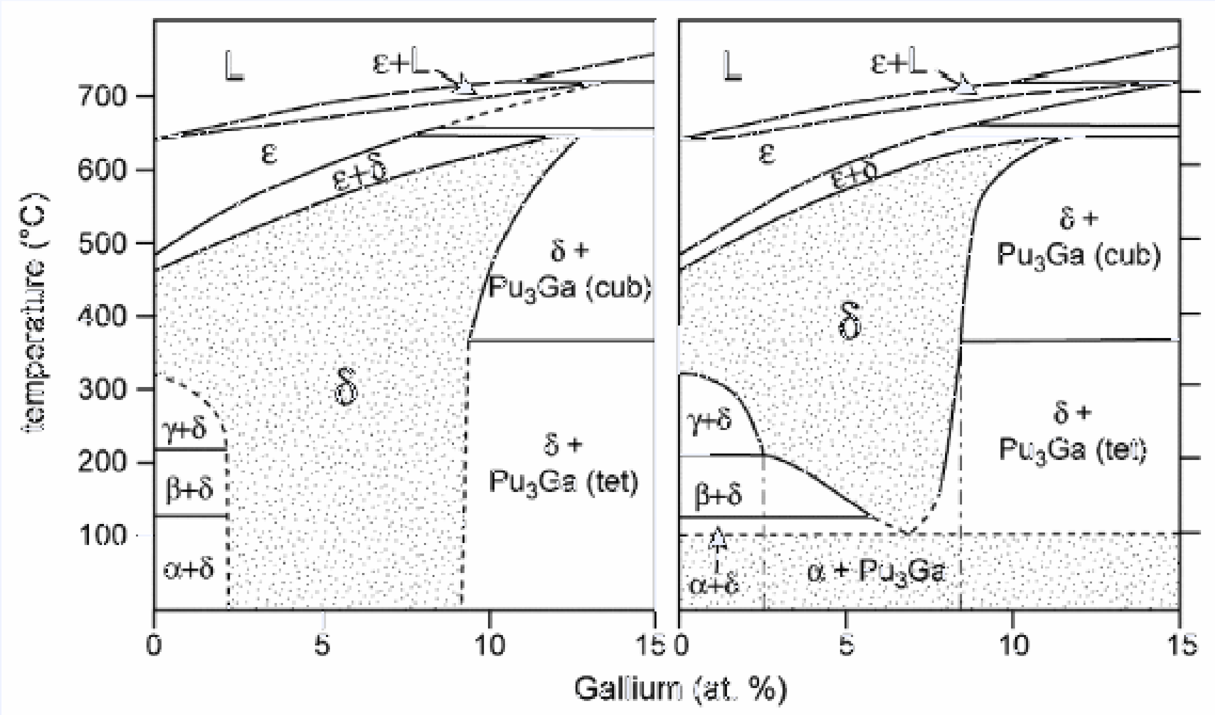
LLNL-CONF-xxxxxx

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

- **Equilibrium phase diagram**
- **5 allotropic phase transformations**
- **Phase transformations and phase stability**
  - **The $\delta \rightarrow \alpha'$ isothermal martensitic transformation**
  - **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**



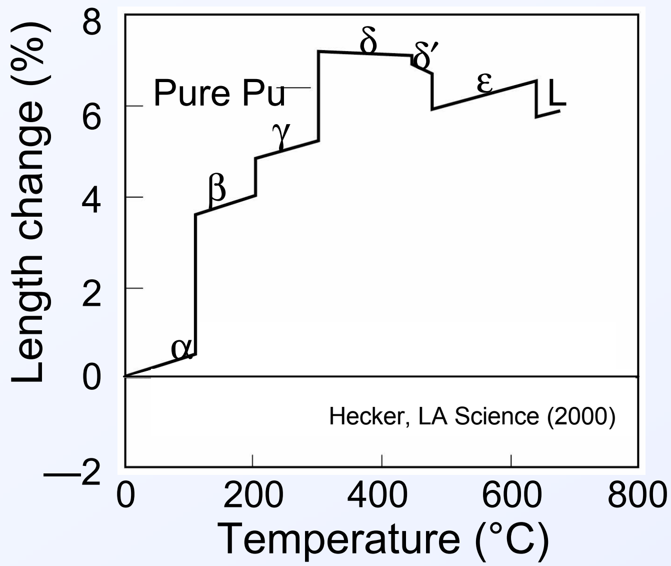
Ellinger, Land, and Struebing, J. Nuc. Mat. (1964)

Hecker and Timofeeva, LA Science (2000)

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

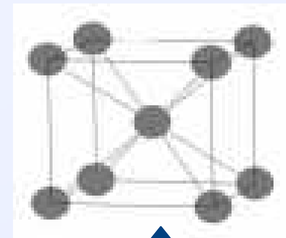
Chebotarev, Plutonium and Other Actinides 1975 (1975)
Adler, Met Trans (1991)
Timofeeva, Aging Studies and Lifetime Extension of Materials (2003)

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



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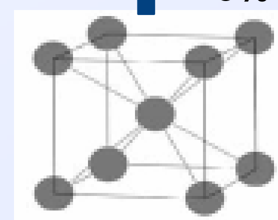
δ′ (468°C - 486°C)
b.c. tetragonal (I4/mmm)
ρ = 16.0 g/cm^3



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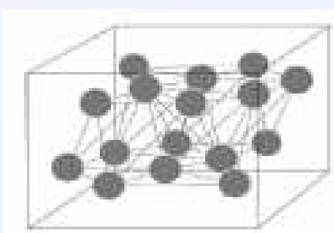

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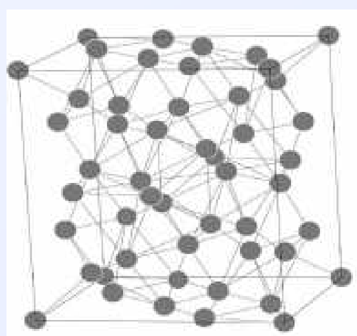

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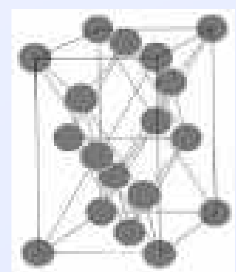

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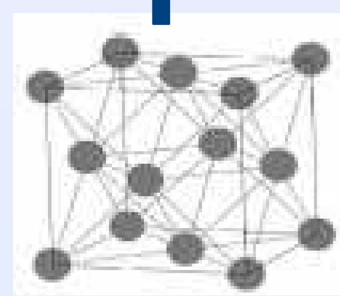


α (Low temperature - 126°C)
monoclinic ($P2_1/m$)
ρ = 19.8 g/cm^3

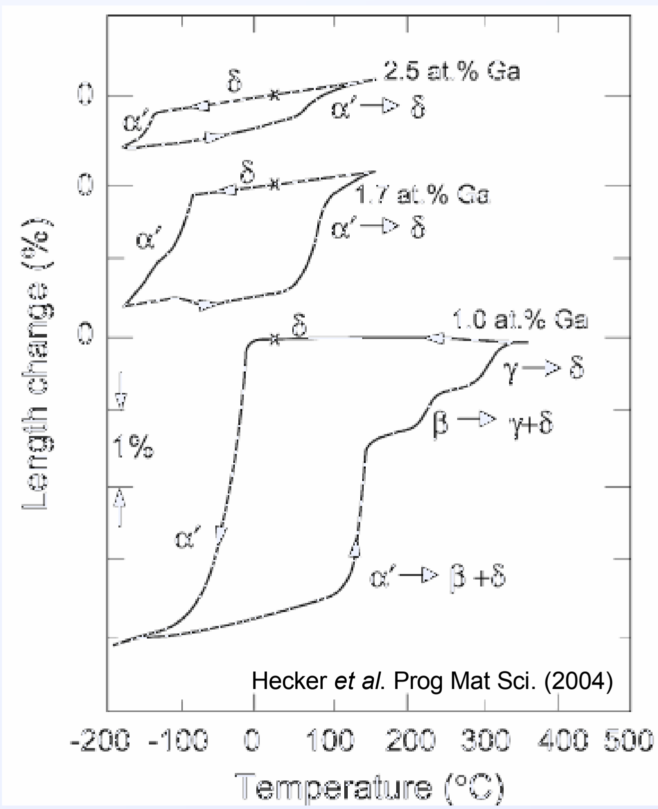
β (126°C - 214°C)
base.c. monoclinic (C2/m)
ρ = 17.8 g/cm^3

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

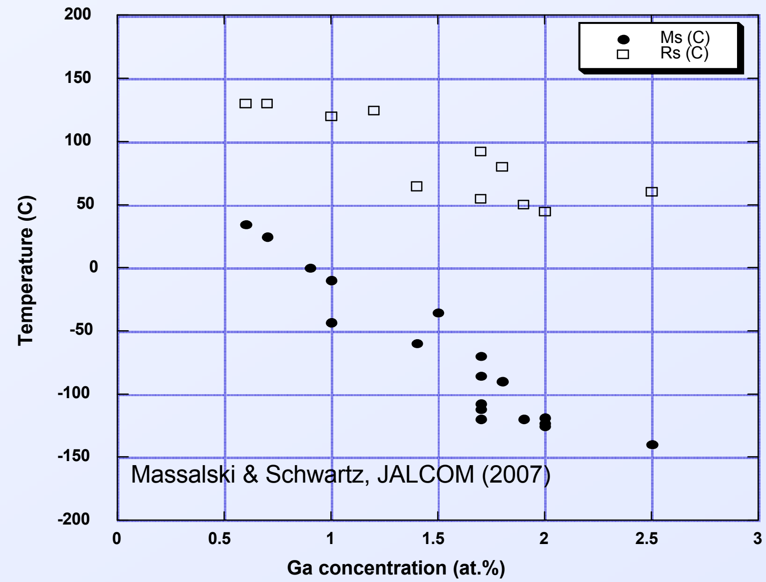
δ (323°C - 468°C)
f.c. cubic ($Fm\bar{3}m$)
ρ = 15.9 g/cm^3

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

The δ → α′ isothermal martensitic transformation can be induced with continuous cooling experiments



The martensite start temperature, M_s is a function of Ga content



Like the δ-phase at room temperature, α′ is also metastable

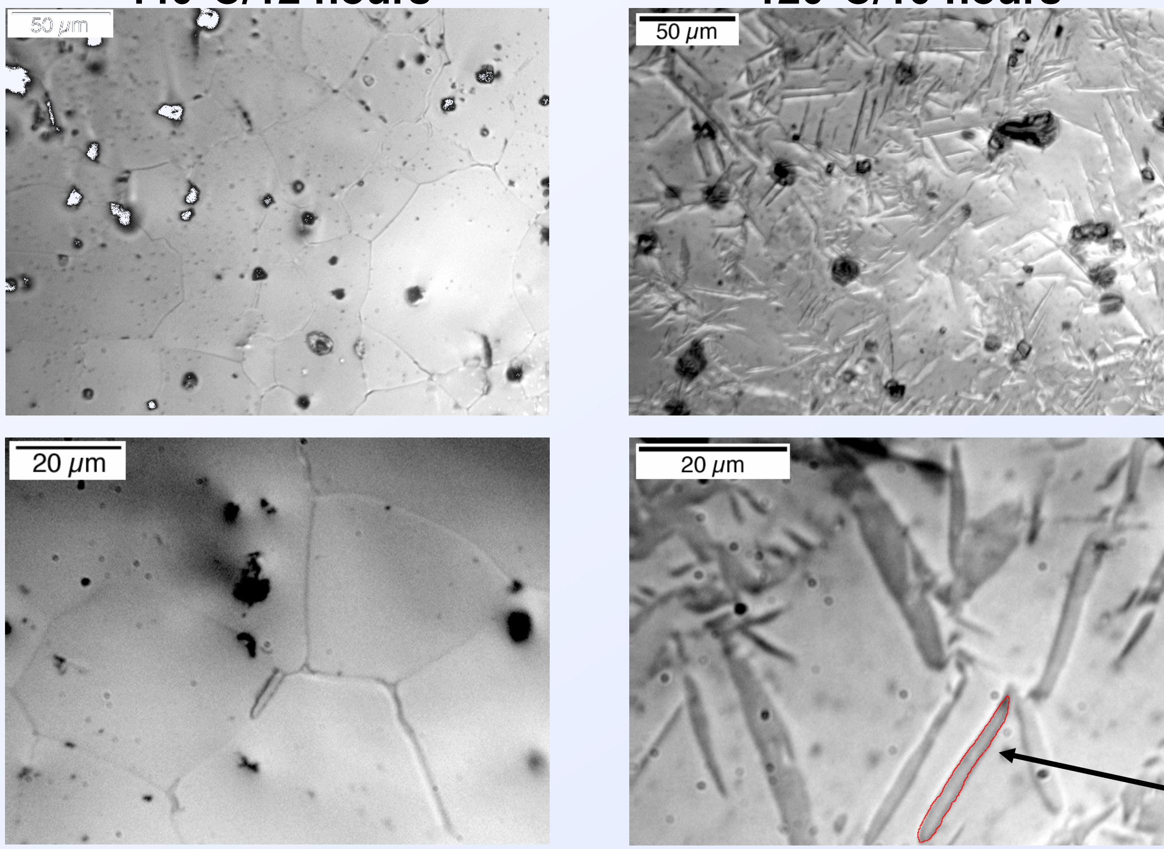
The α′ particles that form from the isothermal martensitic transformation appear as lathes in optical microscopy

Pu - 2.0 at.% Ga

440°C/12 hours

-120°C/10 hours

Untransformed (δ phase)

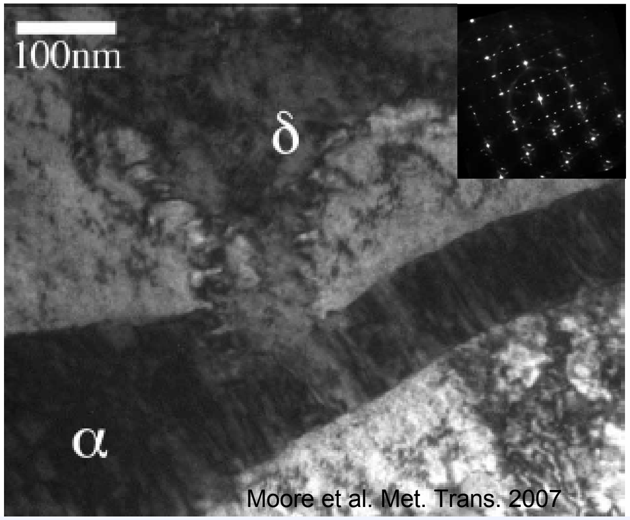


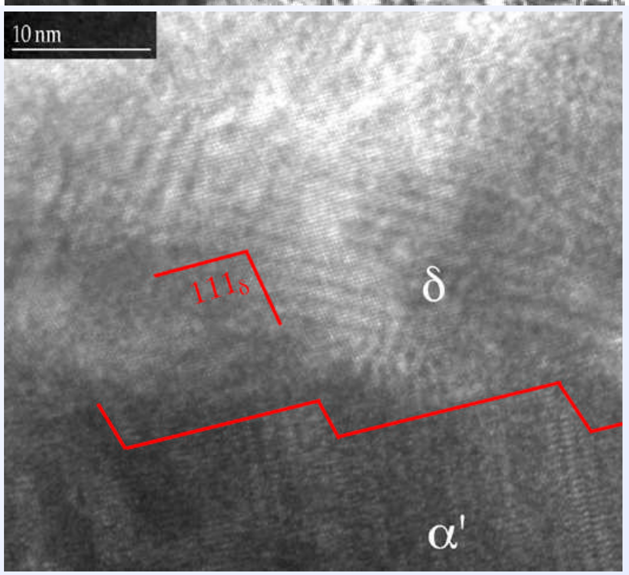
Partially transformed (δ + α' phases)

α' particle

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

The crystallography and morphology of the δ → α′ transformation have been characterized with TEM





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

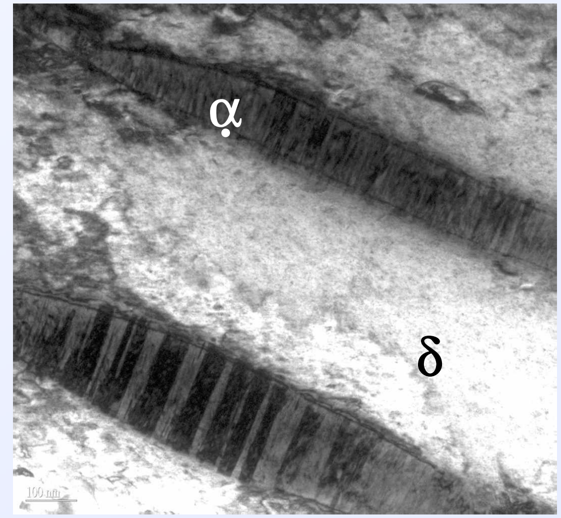
  (Zocco *et al.* Acta Met. 1990)

- **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}**

- **The dislocation density is ~ an order of magnitude greater in the vicinity of α′ particles**



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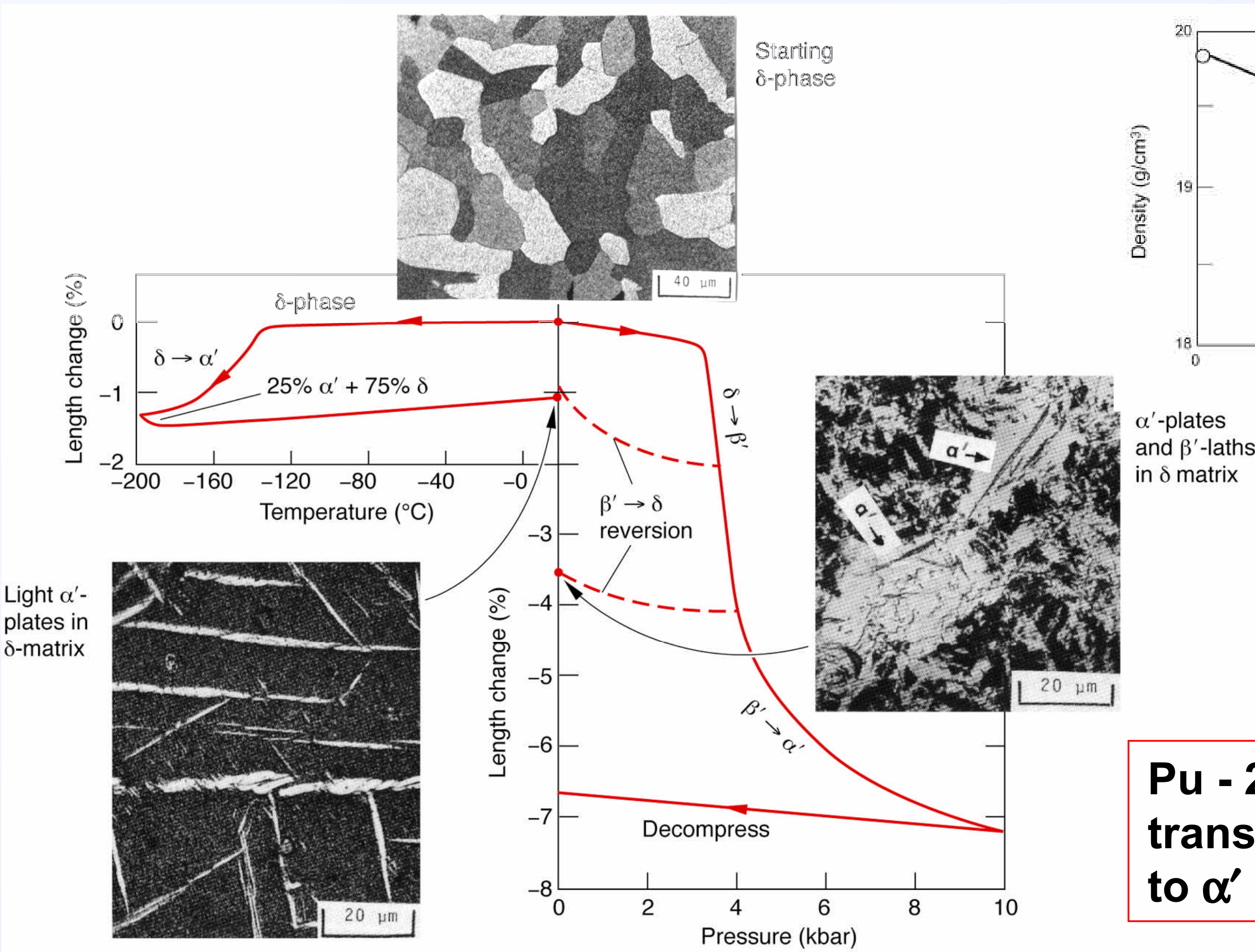
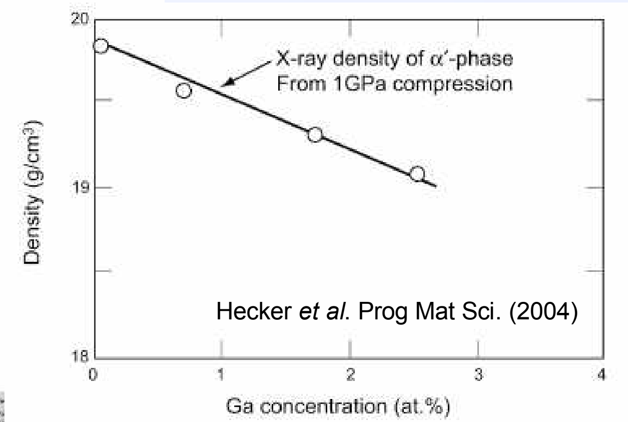
TIFF (Uncompressed) decompressor
are needed to see this picture.

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



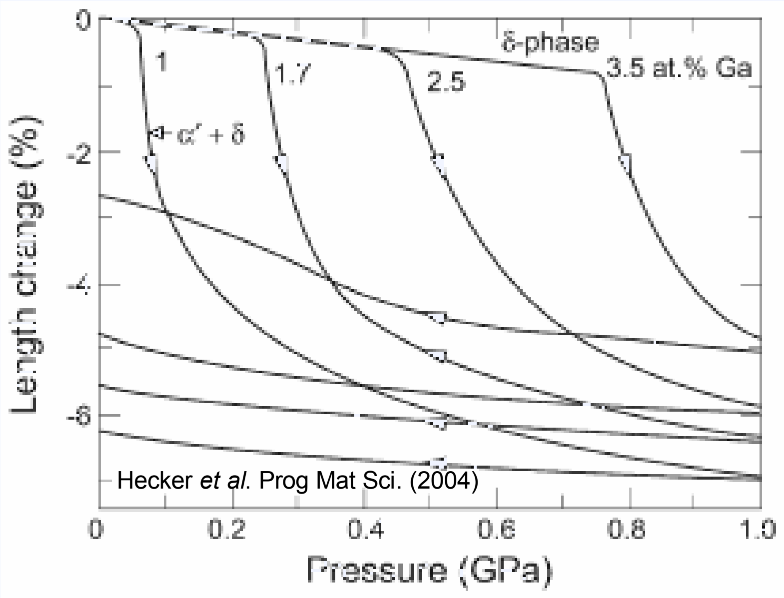


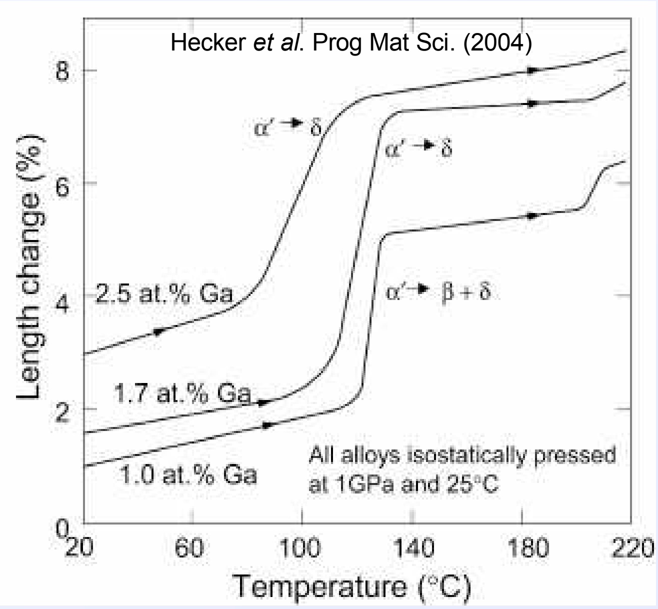
Densities of homogenized Pu-Ga alloys after isostatic pressing to 1 GPa

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

Hecker, MRS Bulletin (2001)

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



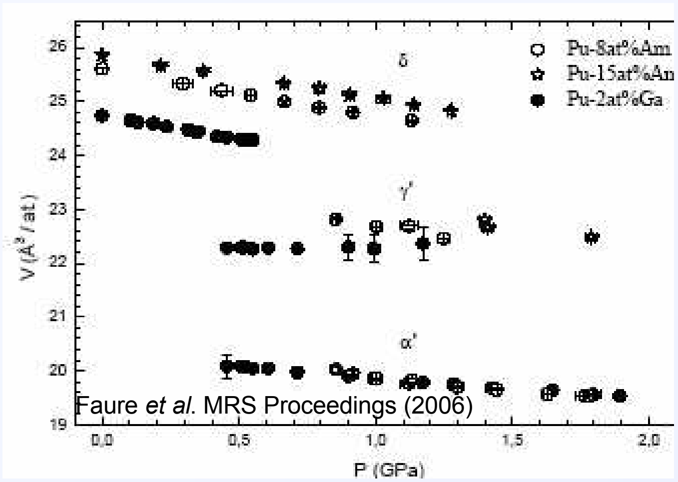


- Under pressure, Pu - Ga alloys transform directly to α′ and undergo either a direct (α′ → δ) or indirect (α′ → β + δ → γ + δ → δ) reversion
- Reversion characteristics are similar to those in thermally-induced transformations

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

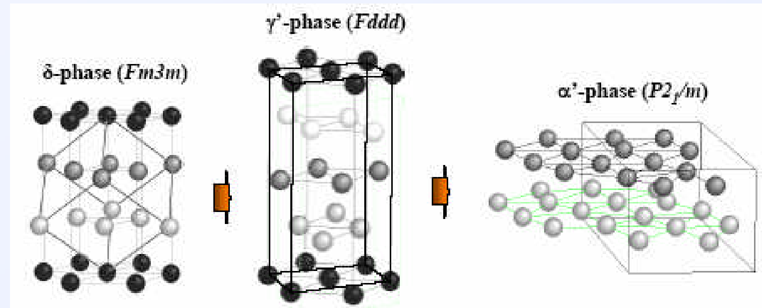
Pressure-induced δ → α′ martensitic transformation

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

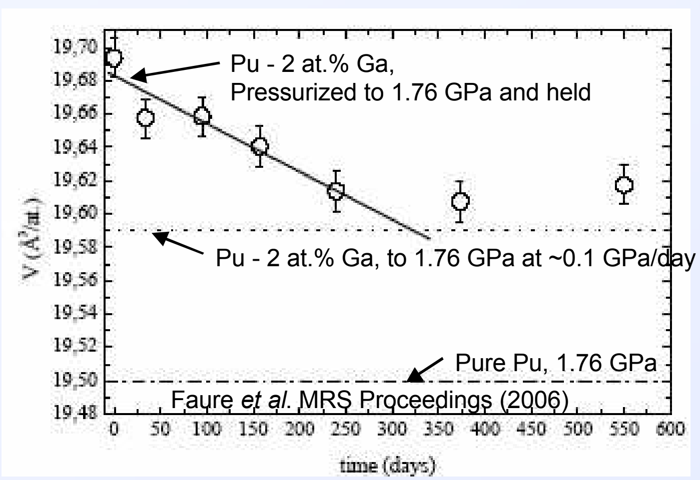


Faure et al. MRS Proceedings (2006)

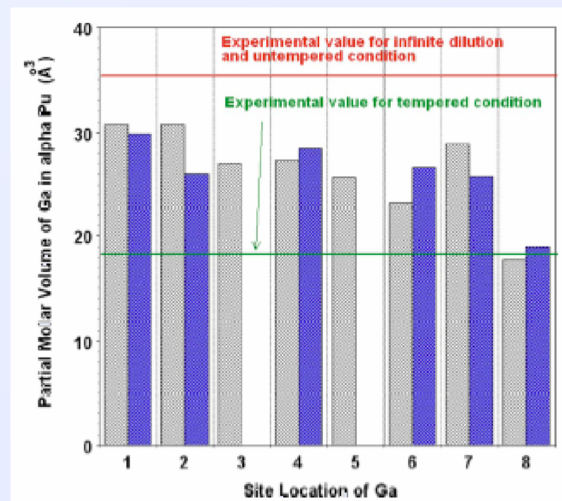
Faure et al. MRS Proceedings (2006)



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



Faure et al. MRS Proceedings (2006)



Sadigh and Wolfer, PRB (2005)

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

Harbur, JALCOM (2007)

QuickTime™ and a
compressed) decompressor
eded to see this picture.

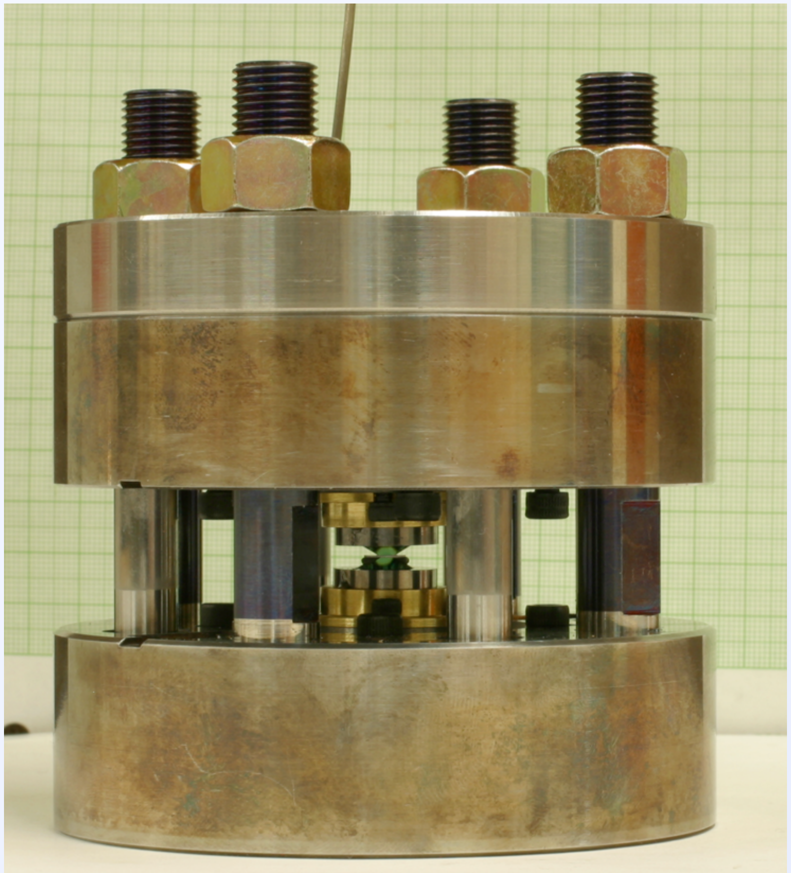
After compressing to 1 GPa

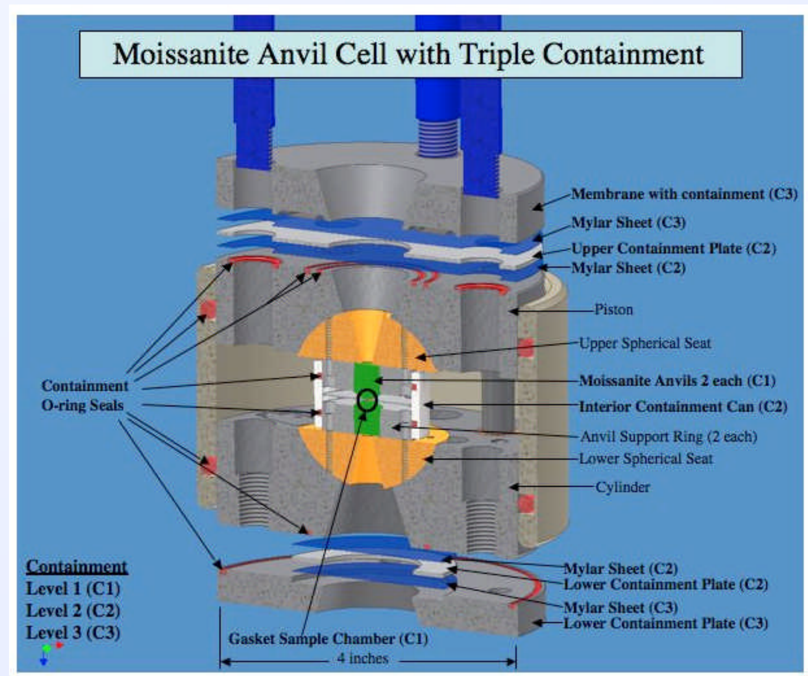
Alloy	% α′	% δ	% amorphous
1.0 at.% Ga	87	0	13
1.7 at.% Ga	66	0	34
2.5 at.% Ga	68	12	20

Harbur, JALCOM (2007)

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

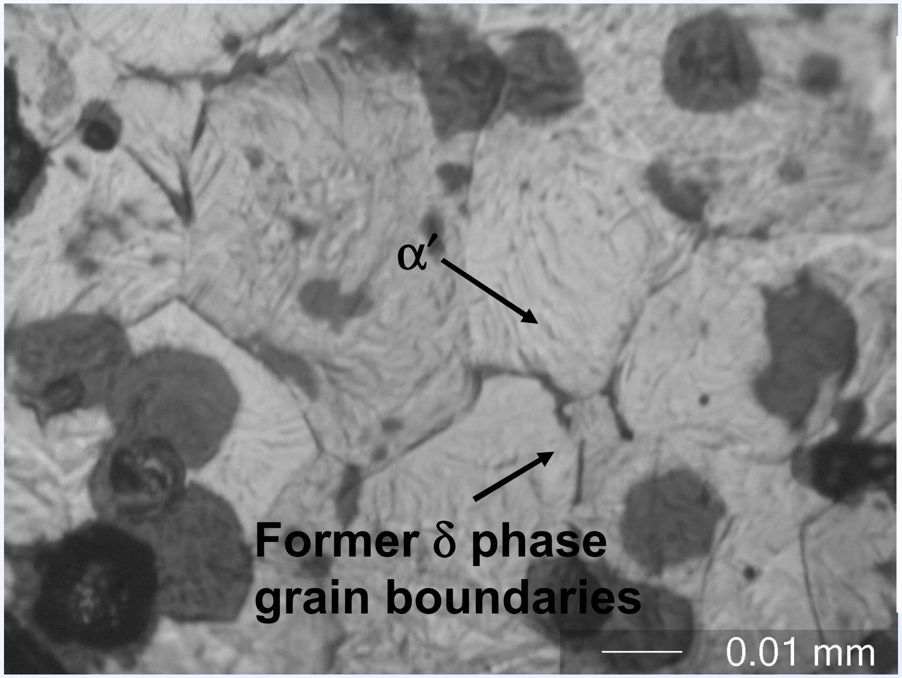
We are coupling low pressure recovery experiments with TEM to elucidate the mechanism and morphology

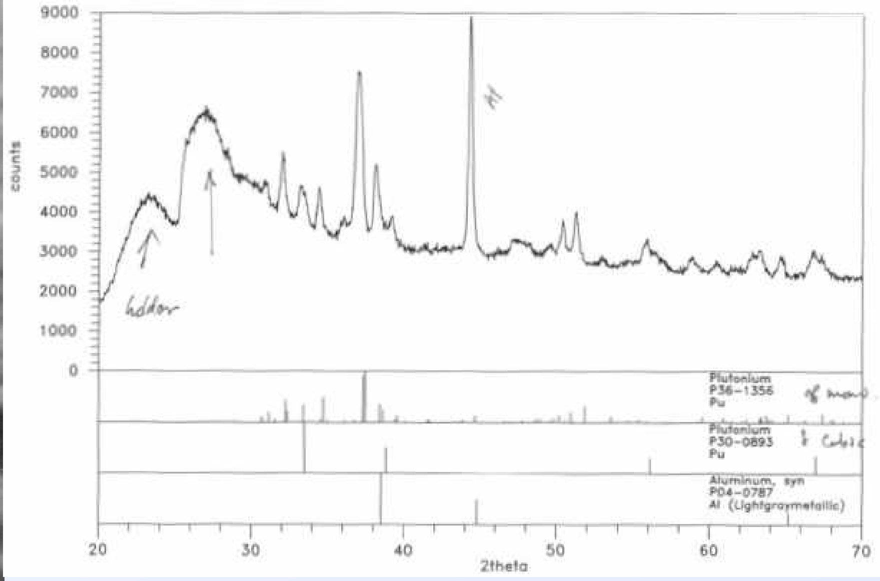




2.3 mm diameter specimens are slowly compressed to 1 GPa in the large volume moissanite anvil cell

Optical microscopy and x-ray diffraction of the compressed specimen reveals α' and δ phase

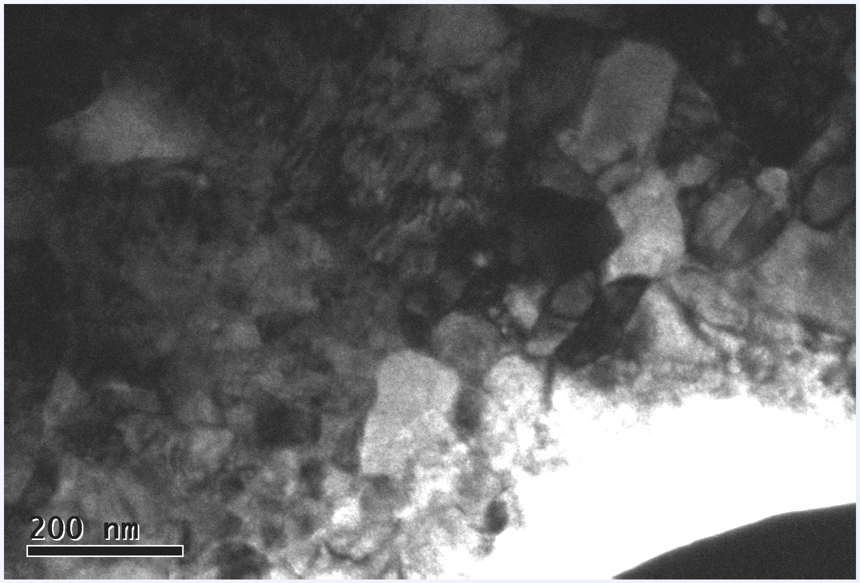


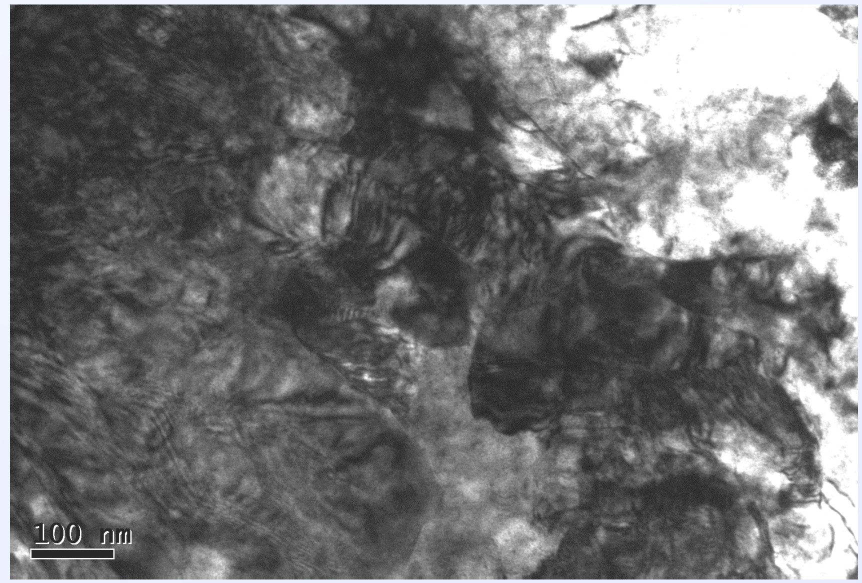


Optical microscopy does not have the resolution to differentiate between phases

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





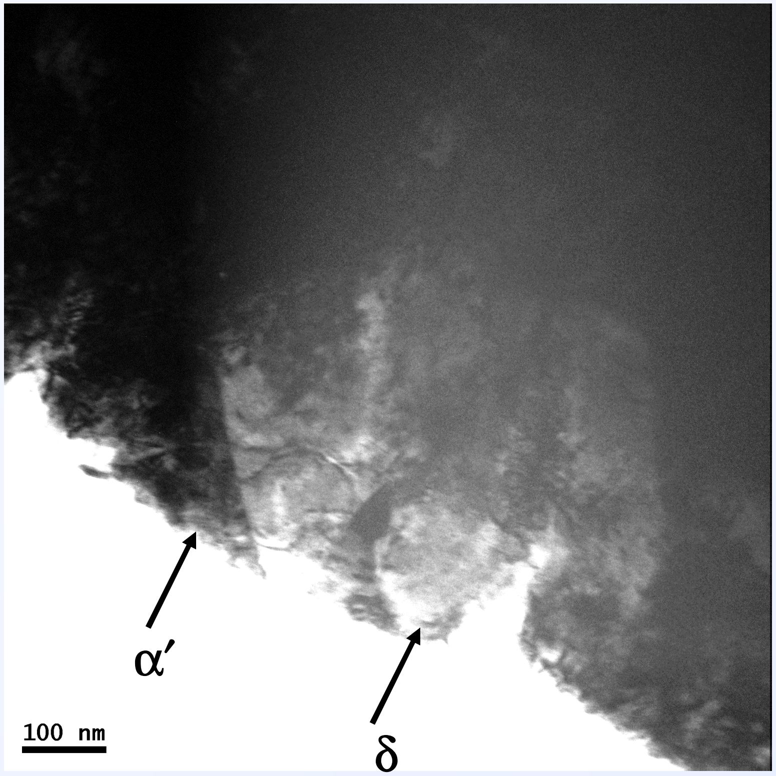
Pressure-induced $\delta \rightarrow \alpha'$ transformation

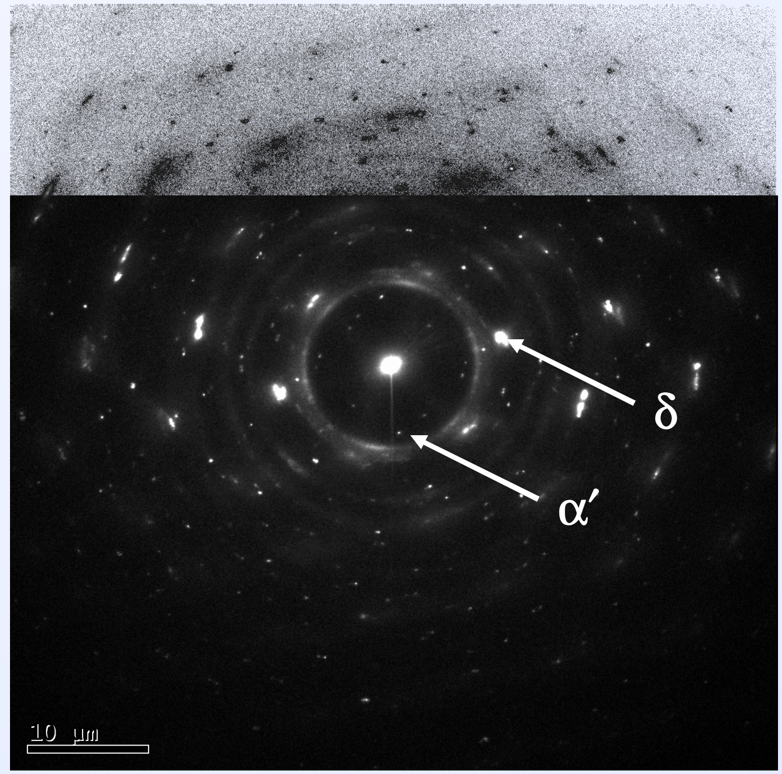
- **Average α' grain size ~ 100s nm**
- **Implies nucleation dominated mechanism**

Low-temperature-induced $\delta \rightarrow \alpha'$ 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



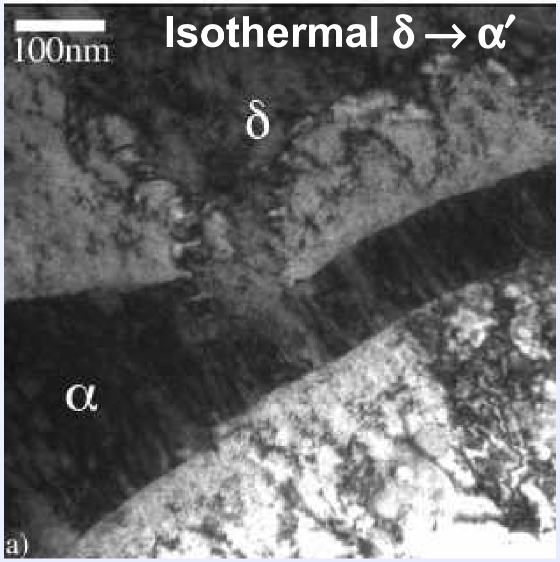


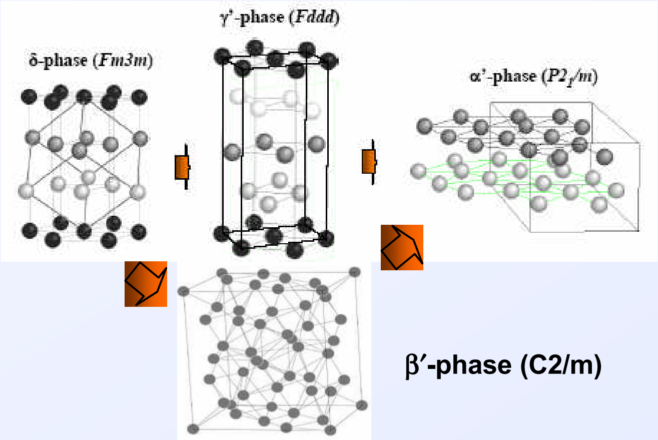
δ phase is observed dispersed between the α′ grains

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

Summary

- Low temperature isothermal $\delta \rightarrow \alpha'$ transformation
  - Nucleation limited
  - Lath-shaped particles
  - Intermediate phases possible
- Pressure-induced $\delta \rightarrow \alpha'$ transformation
  - Nucleation dominated
  - Very fine grain size
  - No evidence of the amorphous phase
  - Intermediate phases likely





β′-phase (C2/m)