LA-UR-03-4111

An Overview of Plutonium Aging

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Los Alamos National Laboratory

Plutonium Futures Conference 2003

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Plutonium Aging Studies

Objectives

- Provide advance warning of manufacturing & aging defects
- Provide a *predictive* lifetime assessment for safety & reliability at a minimum age of 45-60 years

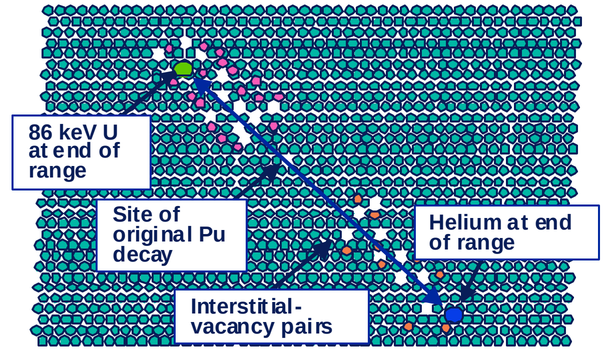

Illustration of alpha-decay in delta Pu, Wolfer (2001)

First LANL Pu-238 spiked delta-Pu casting, May 2002 (Friebert, Olivas, et al)

Approach – Implementing Predictive Science

- Identify Key Material Properties
- Measure properties at zero-age
- Identify aging signatures for key properties and model
  - Accelerate where possible
- Measure aged material, refine models
- Define Thresholds of acceptable change
- Lifetime is defined by point when property reaches limit of acceptable change.

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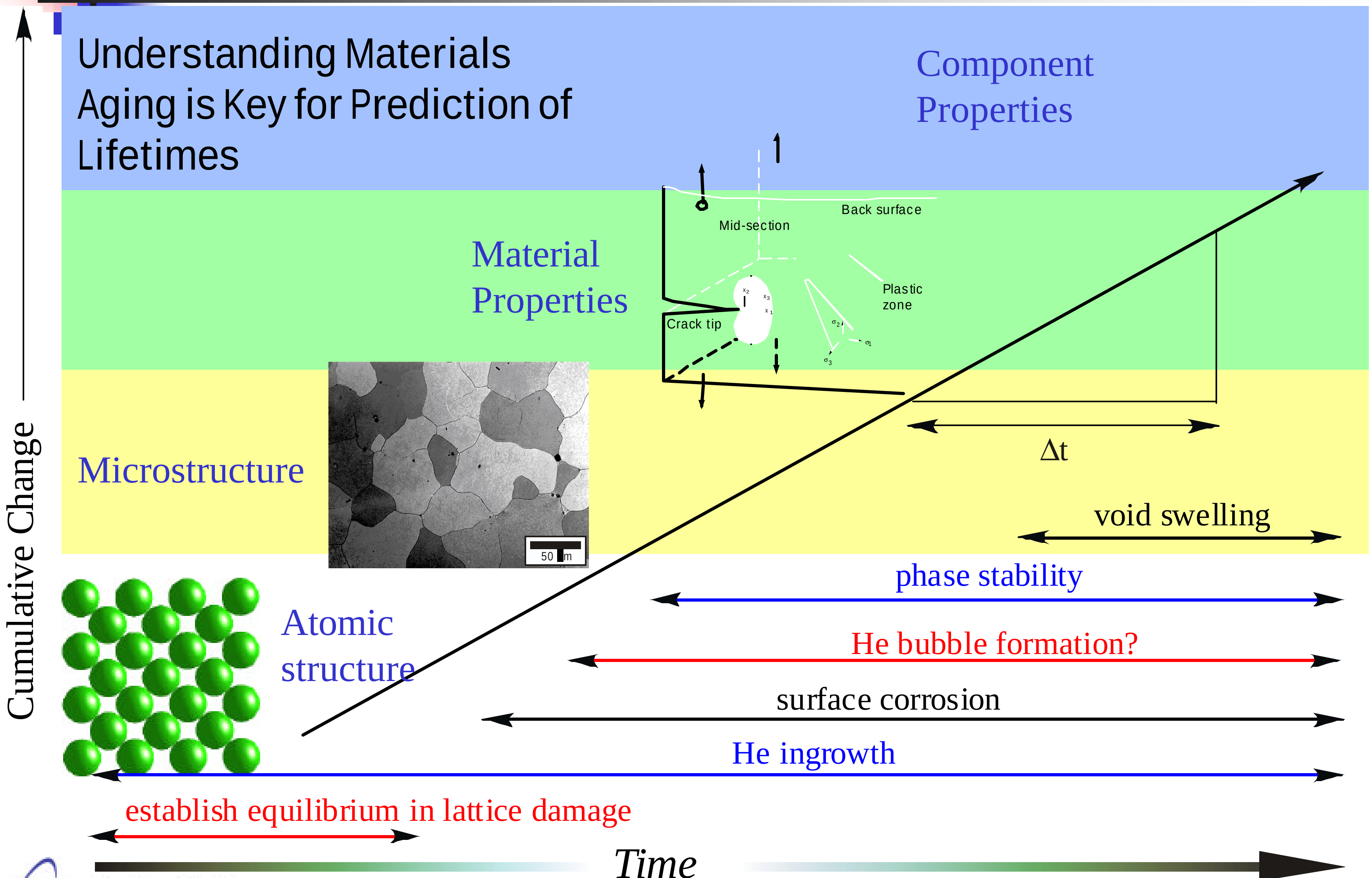
Timescales for Plutonium Aging

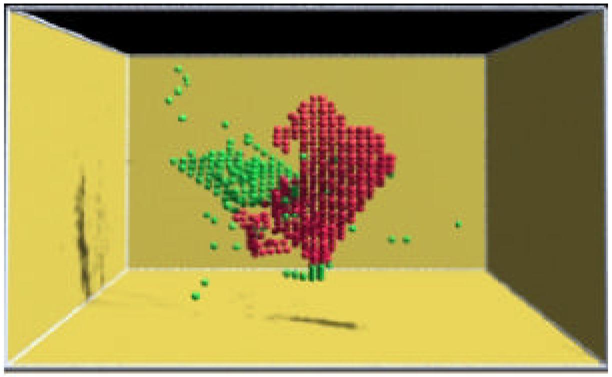


Key Properties and Aging Mechanisms

Key Plutonium Properties

- Density
- Compressibility
- Strength
- Corrosion Resistance

Corrosion of Metallic Pu in a defective Storage Container
(Haschke and Martz, *Plutonium Storage* 1998)



Simulation of radiation damage in delta-Pu
From W. Wolfer, LA Science, vol 26, pp 274 (2000)

Important Potential Aging Mechanisms

- Self-Irradiation Damage
  - He ingrowth
  - change in chemistry
  - atomic displacements from recoil atoms
- Phase Stability
- Surface Corrosion

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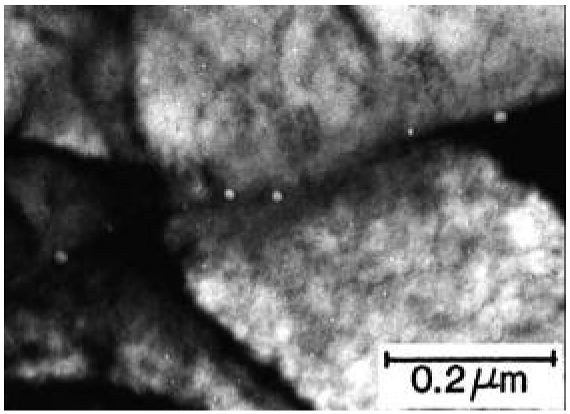
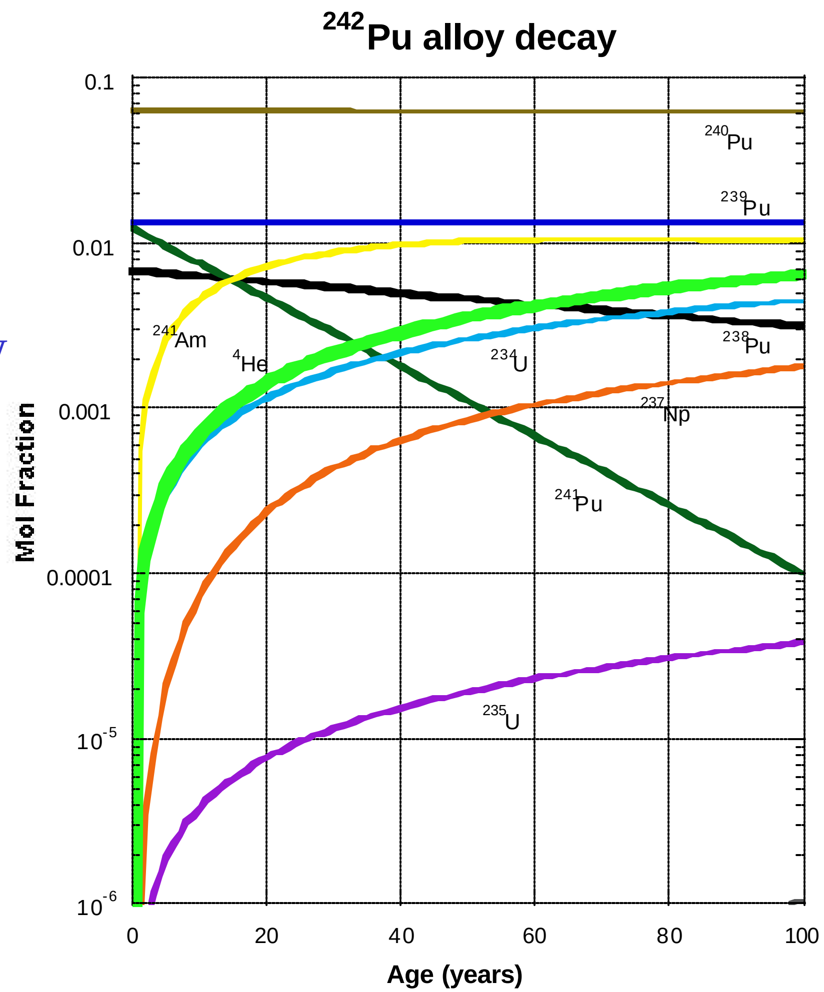
Aging Mechanisms – Self Irradiation & Chemistry

- Chemistry continually changes
  - He ingrowth
    - Potential for bubble growth
  - Am buildup
    - Reaches secular equilibrium in few decades
  - U, Np other important products

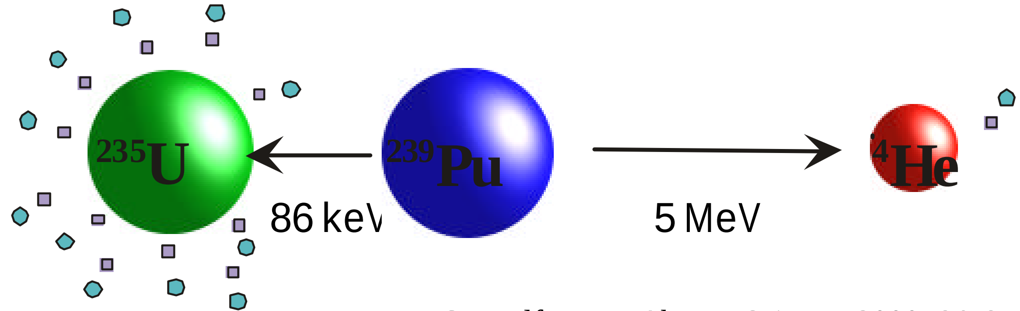


T. Zocco, LANL



Aging Mechanisms – Self Irradiation

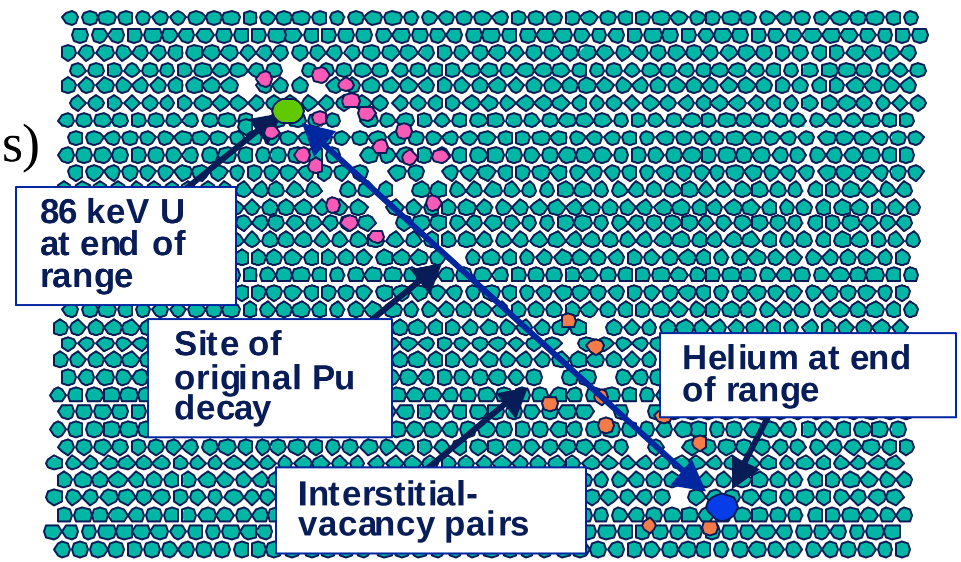
α-decay event



W. G. Wolfer, *Los Alamos Science*, **2000**, *26*, 274

- ^{239}Pu: α-decay: $t_{1/2}$ = 24,000 yr
  - 2.3 x 109 a events/gram/s

- Primary defect production (100 ps)
  - Collision cascade with clustering & recombination
  - ~ 20,000 displacements/event
  - ~ 90% immediately recombine
  - ~ 2500 Frenkel pairs/event
  - 0.1 displacements/atom/year (dpa)



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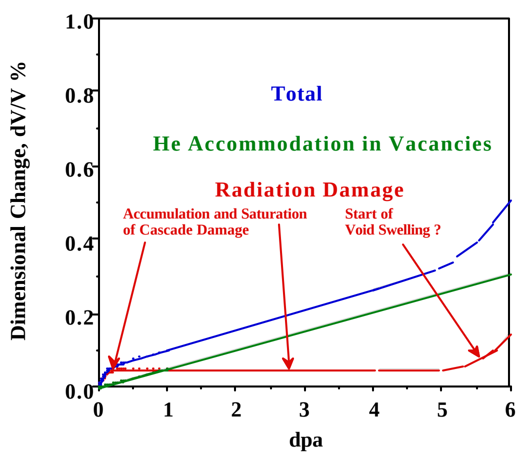
Aging Mechanisms – Self Irradiation

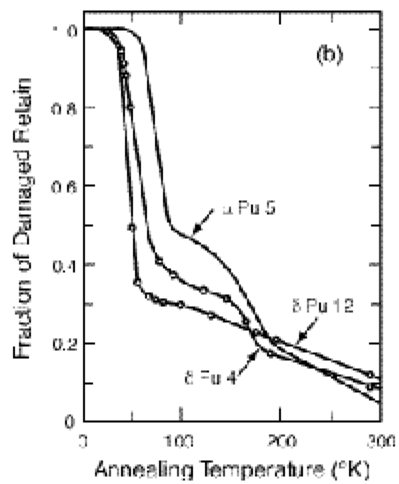
Void swelling is potentially the most important result of self irradiation. The biggest unknown is the magnitude of the incubation period for void swelling.

- Experimental evidence exists for the initial lattice parameter change, and for helium bubble swelling.
- No clear evidence for onset of void-swelling

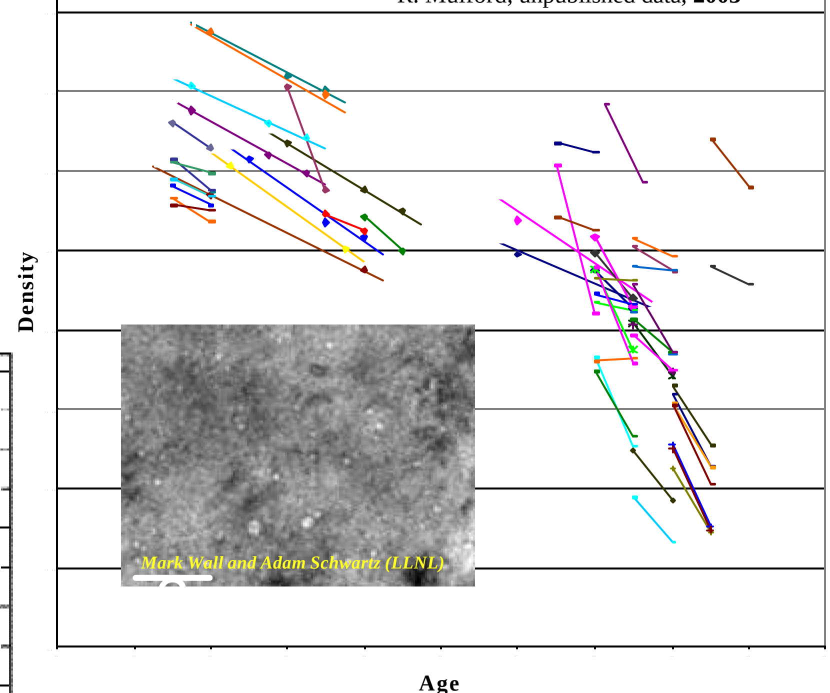


W. G. Wolfer, *Los Alamos Science*, **2000**, *26*, 274

Wigley, D. A., 1965, *Proc. Roy. Soc.* **284A**: 344



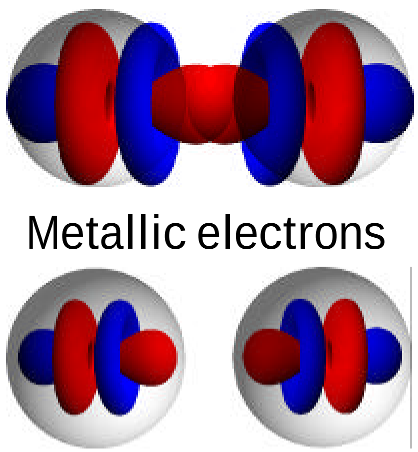
R. Mulford, unpublished data, **2003**



Aging Mechanisms – Self Irradiation

Calculation of displacement requires detailed knowledge of both bond energies and defect structures.

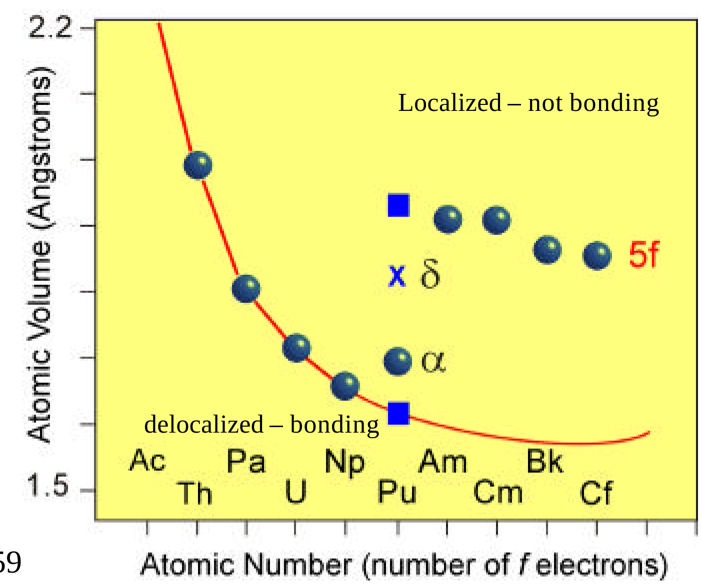
This requires a detailed understanding of f-electrons – a most challenging task!



Metallic electrons

Atomic electrons

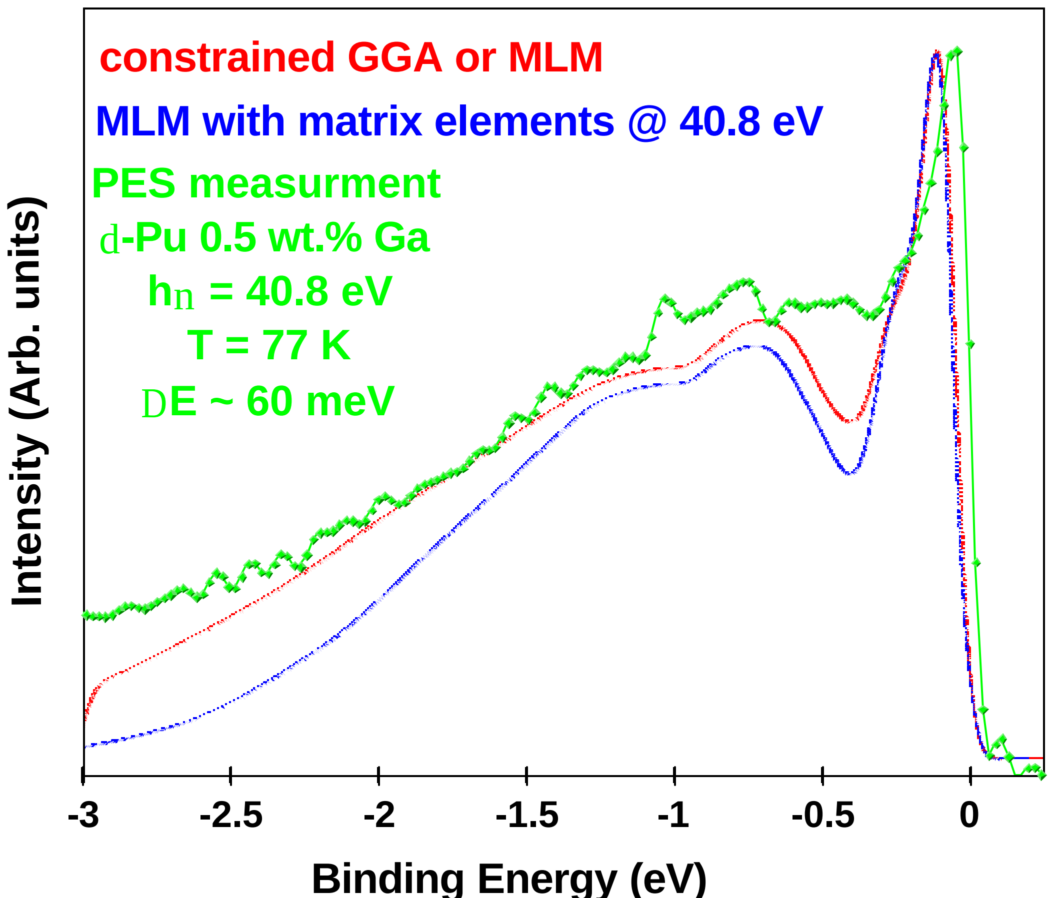
- The transition from delocalized to localized 5f electrons (Mott-like) takes place at Pu
- Pu appears to undergo an intermediate transition that is only partly localized!



Savrasov, Kotliar, Abrahams, *Nature*, **2001**, *410*, 759
Wills, Eriksson, **2000**, *Los Alamos Science*, 26, 128

Aging Mechanisms – Self Irradiation Damage

d-Pu Photoemission Data, Electronic Structure Calculations and Matrix Elements at 40.8 eV

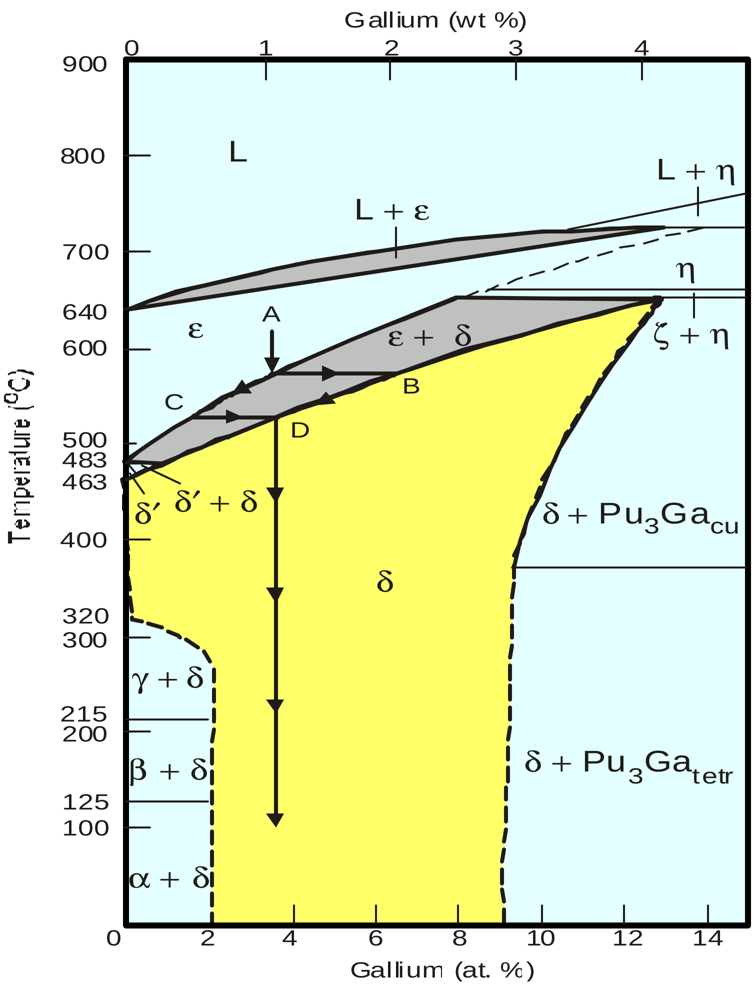


New Developments in Electronic Structure Calculation

- Photoemission data taken at a photon energy of 40.8 eV.
- Matrix element calculations between the initial and final states using a photon energy of 40.8 eV.
- One-electron calculations fail to account for 5f electron correlations
- Electronic structure calculation using the constrained GGA or mixed-level model (MLM) with 4 of the 5 Pu 5f electrons localized.

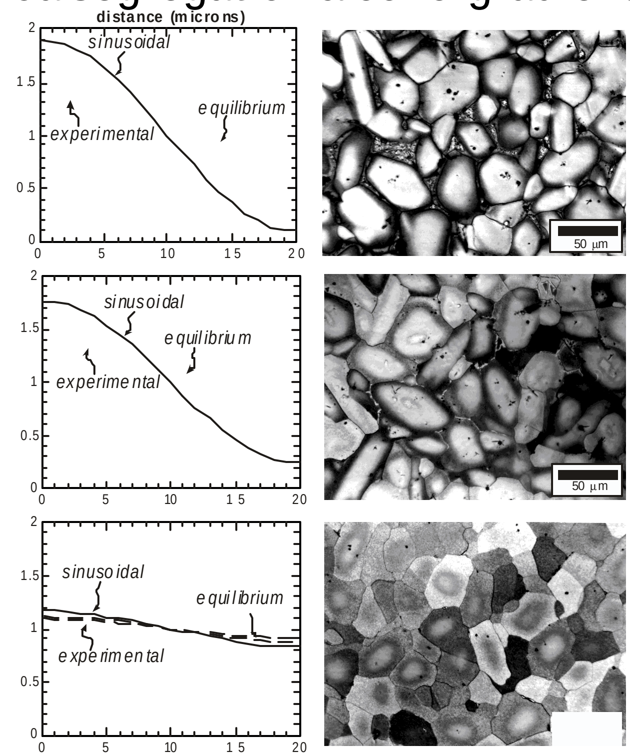
J.J. Joyce, L.A. Morales & J.M. Wills

Aging Effects: Phase Stability



Ellinger, *J. Nucl. Mater*. **1964**, *12*, 226

Ga segregation & conc. gradients



J. N. Mitchell, F. E. Gibbs, T. G. Zocco, R. A. Pereyra, *Met. Mater. Trans* **2001**

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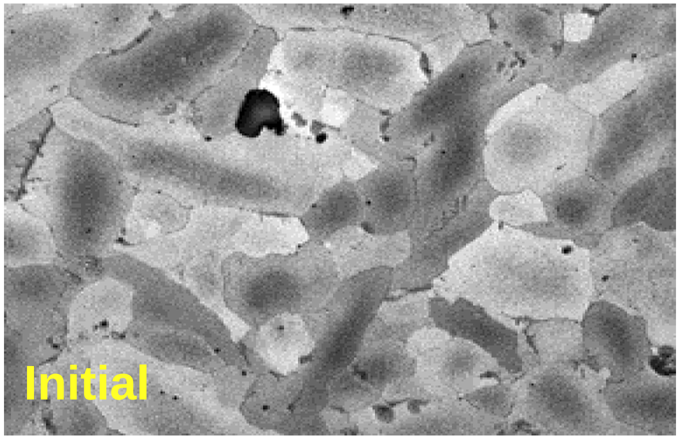
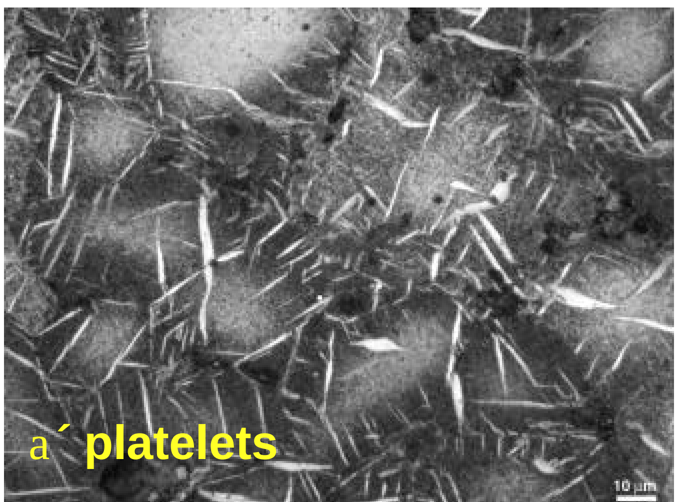
Aging Effects: Phase Stability

The d →a¢ Transformation in Pu-0.5 wt. % Ga

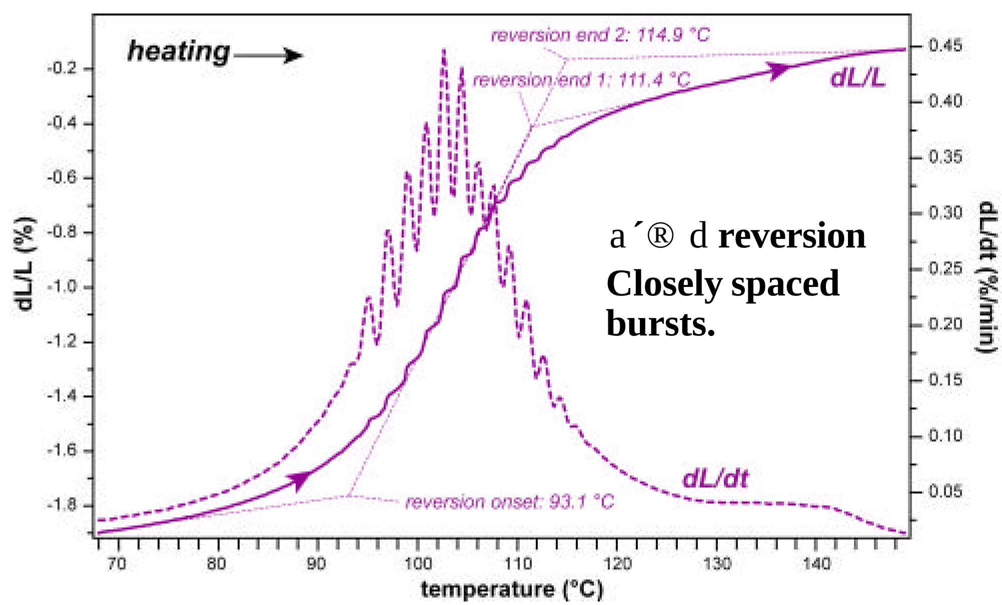




25 °C ® -155°C ® 25 °C

- Composition
- Thermal history
- Aging
- Microstructure
- Processing

Dilatometry

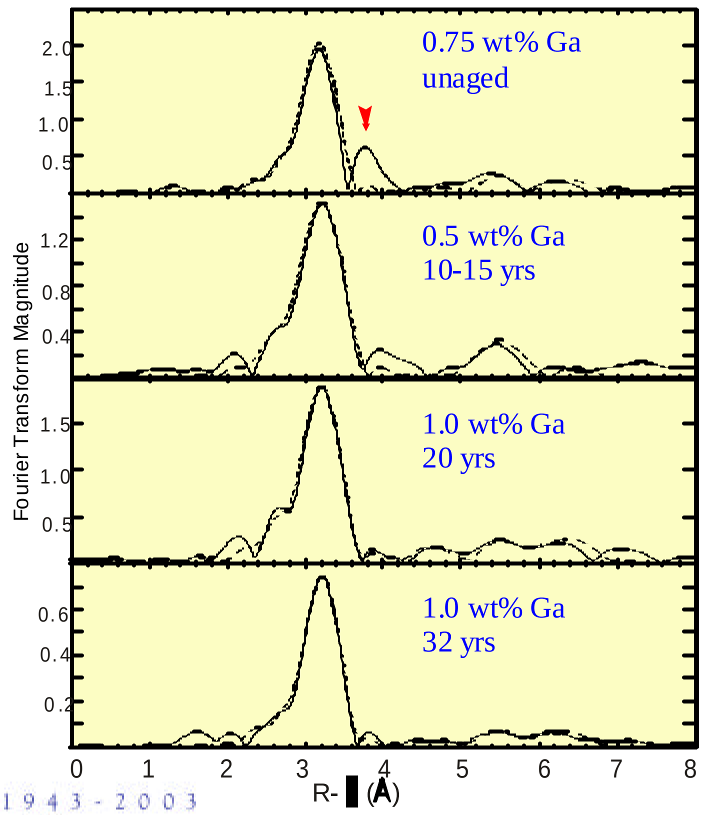


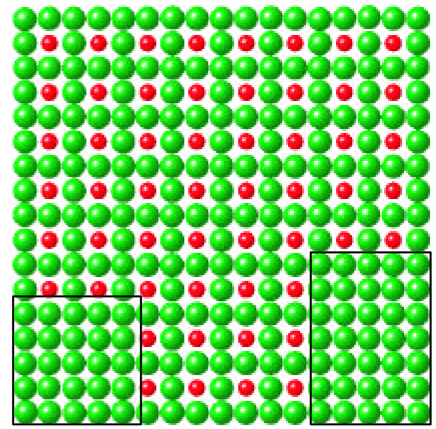
J.Mitchell, R. Pereyra

Phase Stability: XAFS Results and Local Order

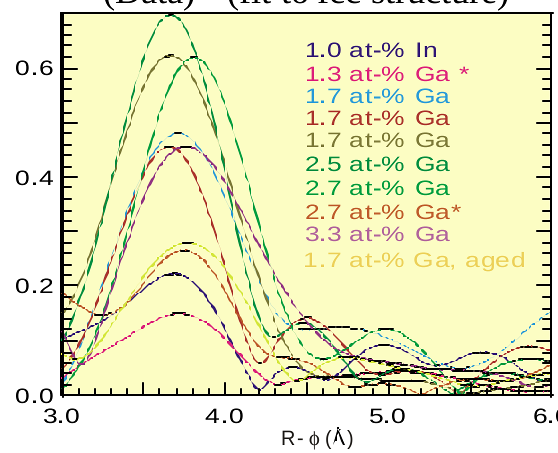
- Unaged alloys near metastable composition range higher degree of disorder
- Aged materials or high stabilizer concentration show higher degree of order
- Radiation damage may redistribute Ga with age

EXAFS Fourier Transform





(Data) - (fit to fcc structure)



S.D. Conradson, L.E. Cox, B. Martinez, L. Morales and R.A. Pereyra

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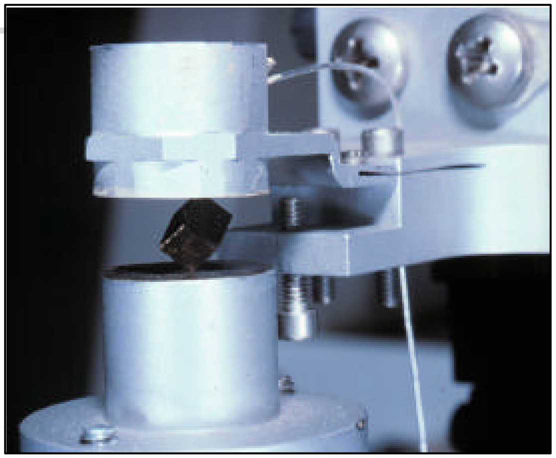
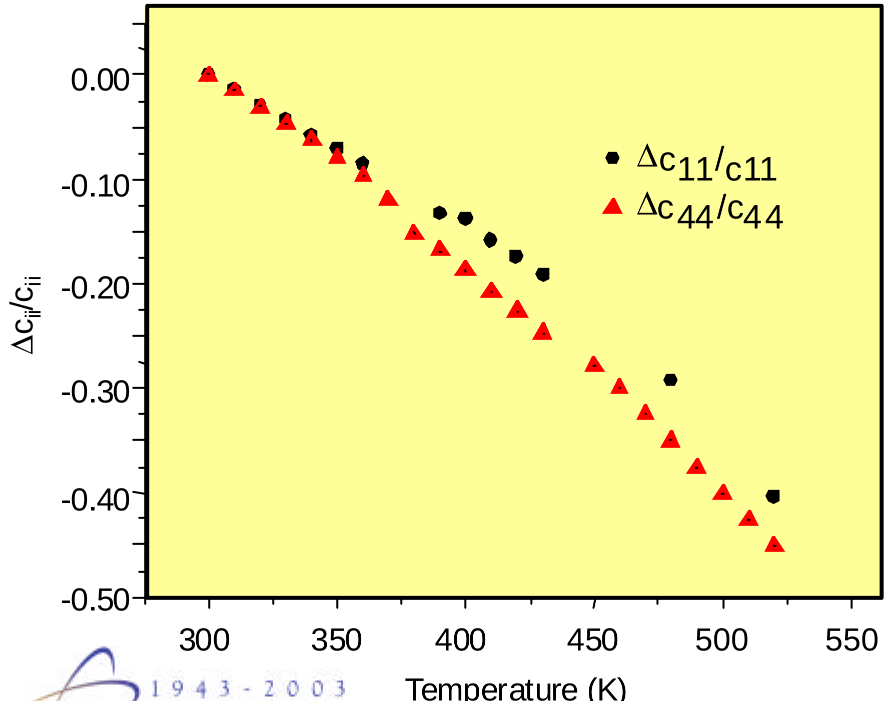
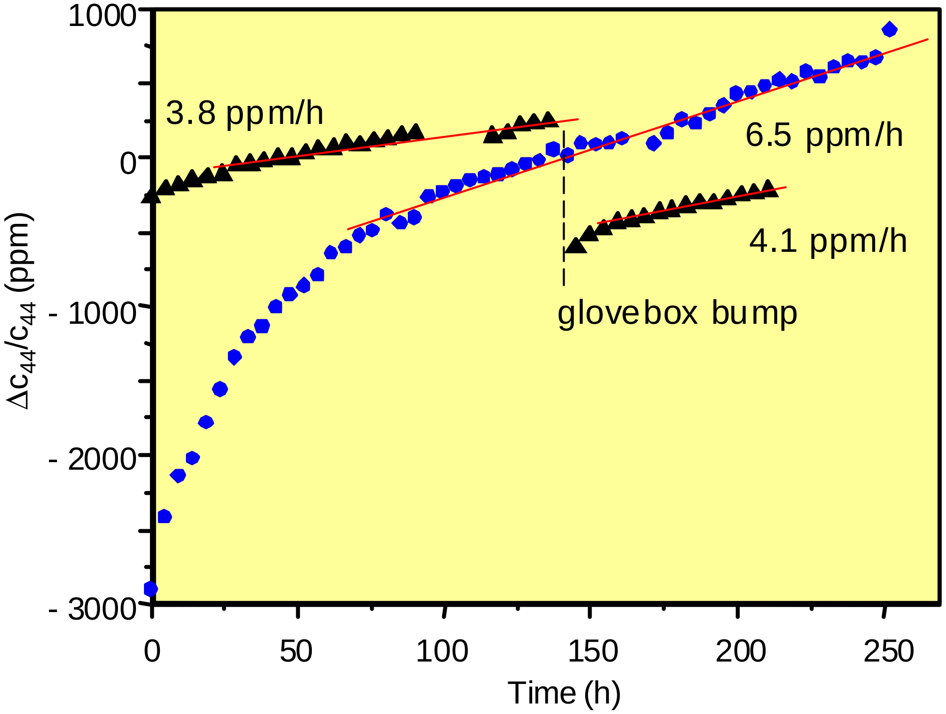
Phase Stability: elastic constants as an early indicator

- Can determine full elastic tensor for EOS
- Phase stability (α-δ transition) can readily be observed using RUS
- Real-time aging effects probed
  - **t = 0y; B = 29.6 GPa**
  - **t= 15 y; B = 34.3 GPa**



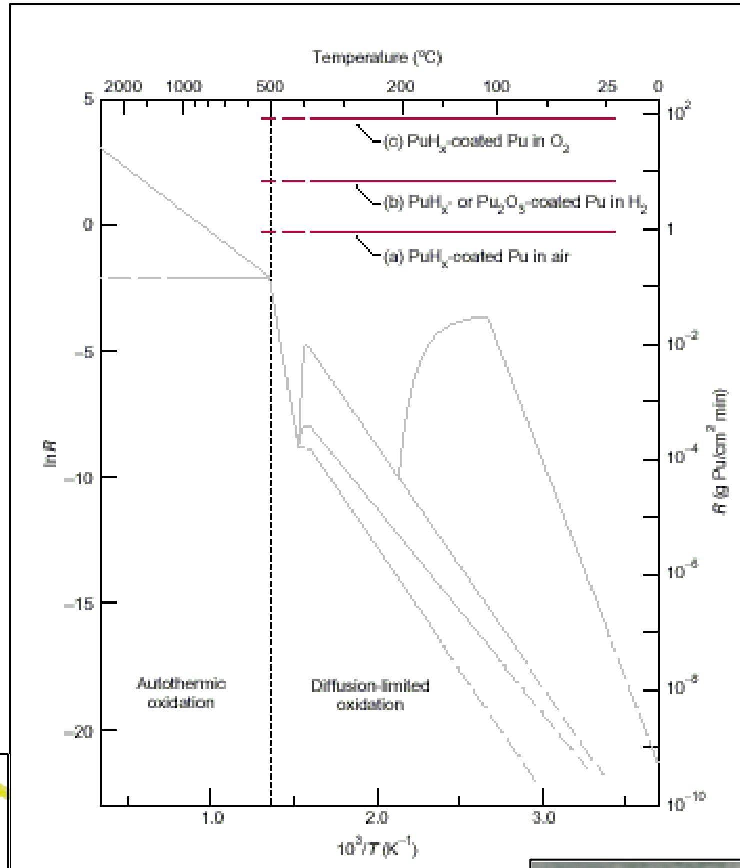




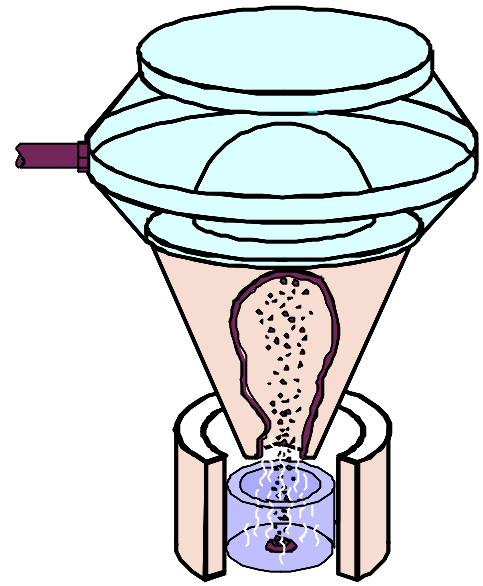
A. Migliori, J. Baiardo, B. Martinez, and R.A. Pereyra

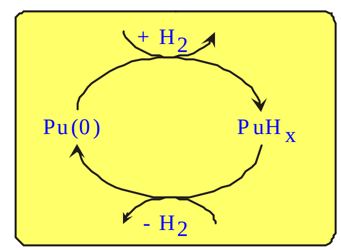
Surface Corrosion: hydrogen-catalysis accelerates reaction

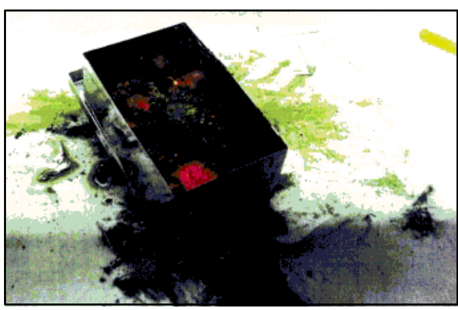
- Hydride-catalyzed reactions are potentially catastrophic
  - high rates can be useful for recovery or processing of metallic Pu
- Pyrophoric behavior at elevated temperatures (>500 C)
- Prevent by 2-methods:
  - seal containers
  - exclude organics



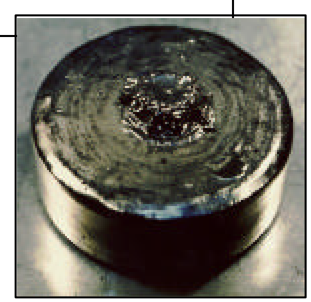
Haschke, Allen, Morales, **2000**, *Los Alamos Science*, 26, 252





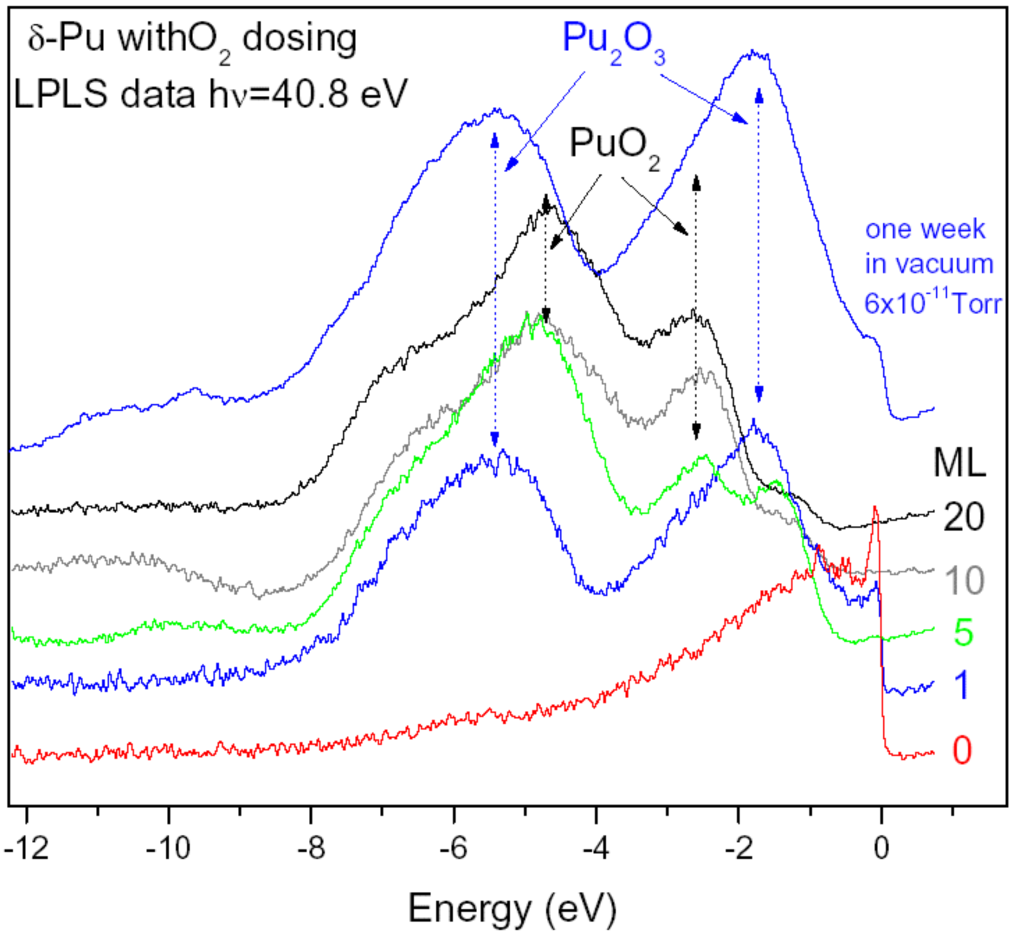


Stakebake 2001

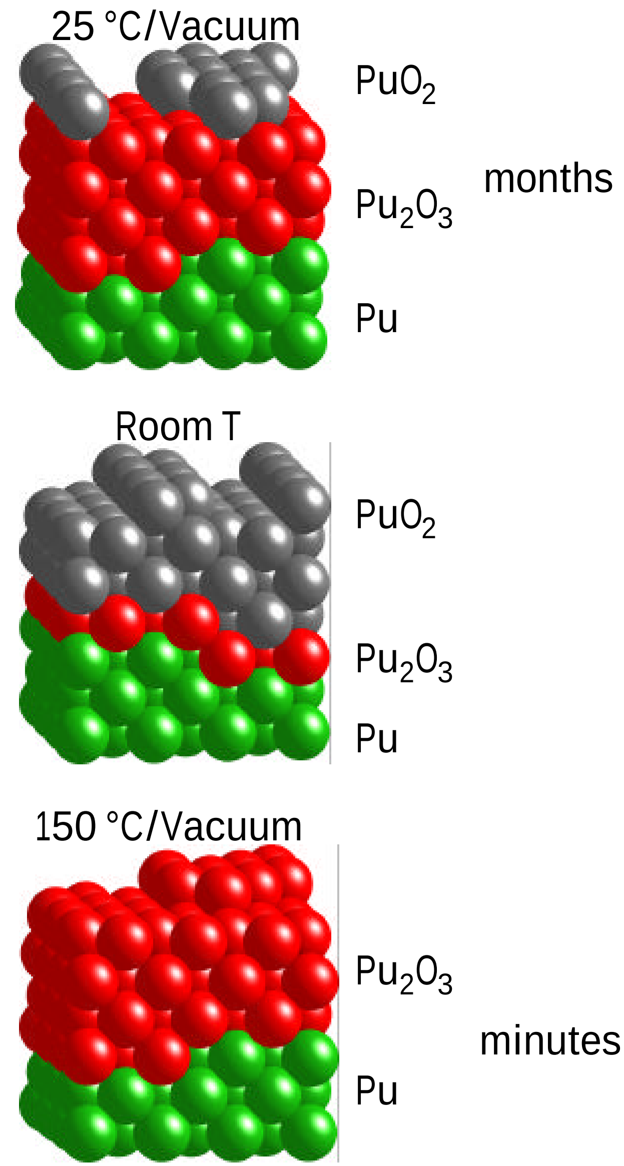


Surface Corrosion: the complexity of surface oxides

Photoemission: O_2 on d-Pu



J.J. Joyce & L.A. Morales



Surface Corrosion: catalyzed oxidation

Catalyzed oxidation in storage has lead to container failure and breach

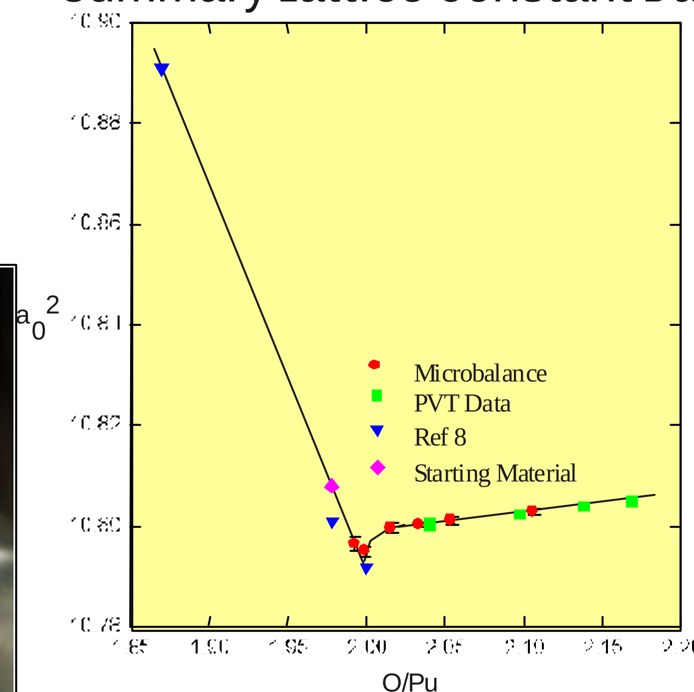
- small molecule reactions have led to stoichiometry changes, containment breaches and dispersal of material (safety concern)

Haschke & Martz, *Los Alamos Science*, **vol 26**, *266*

- PVT, TGA microbalance, MS, and XRD studies suggest formation of a higher oxide

$$PuO_2(s) + xH_2O \longrightarrow PuO_{2+x}(s) + H_2(g)$$

Summary Lattice Constant Data



Haschke, Allen, Morales, *Science*, **2000**, *287*, 285

Plutonium Aging: Some Preliminary Conclusions

Conclusions

- Virtually all conditions in Pu are "ripe" for aging damage
- Yet, we have found no first-order effects after decades
- Surface reactions are potentially most catastrophic
- Phase stability is still a concern over full range of expected conditions, especially for some alloys
- We are beginning to measure lattice damage and helium accumulation effects
- Void swelling may cause largest density change - incubation period is very sensitive to defect structure
- We still have very little information on mechanical properties and dynamic response
- He in-growth is still a concern, especially at extended ages

Acknowledgements

Steve Conradson	**John Joyce**
Luis Morales	**John Wills**
Jeremy Mitchell	**Al Migliori**
Barbara Martinez	**Larry Cox**
Robi Mulford	**Adam Schwartz**
Tom Schepp	**Sig Hecker**
Franz Friebert	**Dave Olivas**
Dave Dooley	**Brad Storey**
Heather Hawkins	**Roland Schulze**
John Haschke	**Tom Allen**

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