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Toward an understanding of aging in plutonium from direct measurements of stored energy

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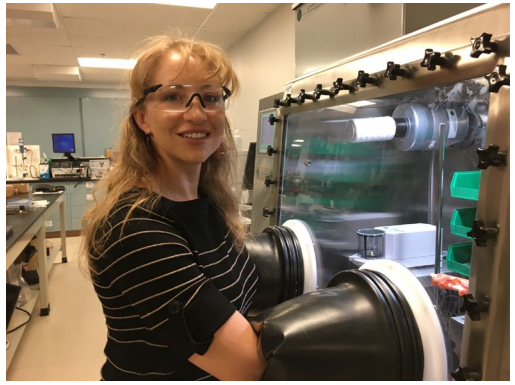
Sue Ennaceur



Alex Marchi

Mark Wartenbe

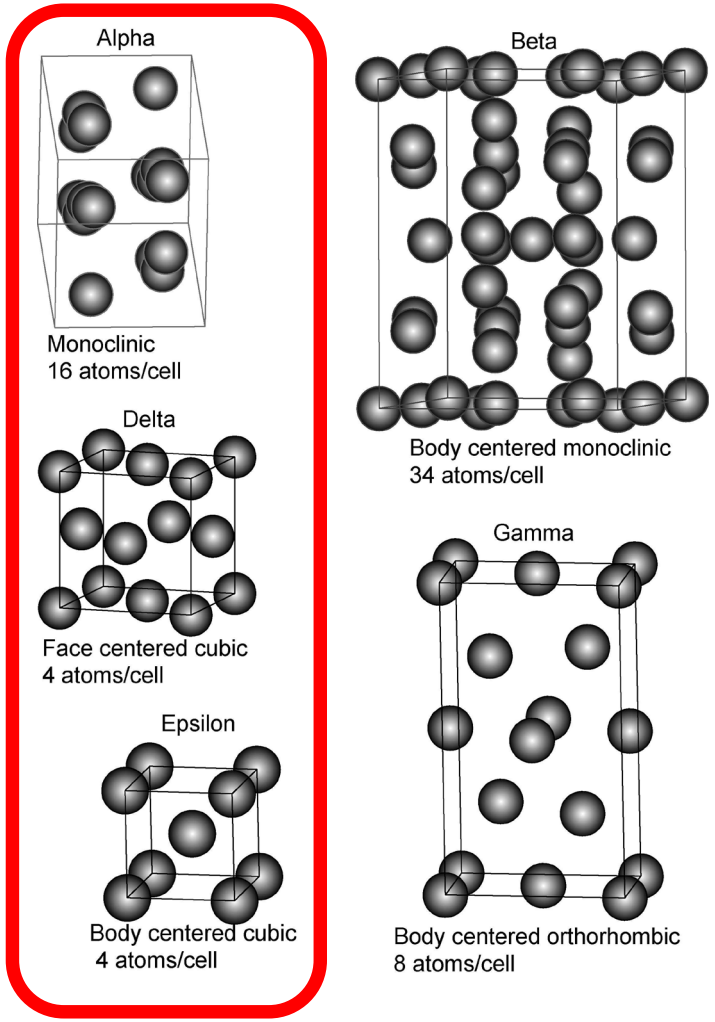
Troy Semelsberger

Albert Migliori

What we will show

- Plutonium has a propensity to make short bonds. Pu is its own impurity—Lawson calls it a self-intermetallic.
- What we are sure of and what is suspect in observing aging.
- Short-bond Pu defects lead to a workable quantitative model of aging.
- The model is falsifiable; we make testable predictions.

δ-plutonium has differences from other fcc metals that have been overlooked in attempts to understand damage



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Pu as its own impurity (1)
The thermodynamically-stable α–phase at room temperature has two groups of bonds

Table 10. *'Short' and 'long' bonds* (Å)

Atom type	Short bonds No.	Short bonds Range	Long bonds No.	Long bonds Range	All bonds No.	All bonds Mean length
I	5	2·57–2·76	7	3·21–3·71	12	3·10
II	4	2·60–2·64	10	3·19–3·62	14	3·21
III	4	2·58–2·66	10	3·24–3·65	14	3·18
IV	4	2·58–2·74	10	3·26–3·42	14	3·13
V	4	2·58–2·72	10	3·24–3·51	14	3·19
VI	4	2·64–2·74	10	3·21–3·65	14	3·22
VII	4	2·57–2·78	10	3·30–3·51	14	3·15
VIII	3	2·76–2·78	13	3·19–3·71	16	3·32

- At room temperature, Pu wants to be α.
- Unlike other fcc and bcc metals, defects and radiation damage in δ–plutonium have an "escape route" into short bonds.
- Short bonds can absorb radiation damage and thermal defects easily.

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Pu as its own impurity (2)
δ'–Pu likely not a phase but a route to easy-to-make short bonds

Table 3.1–CRYSTAL STRUCTURE DATA FOR PLUTONIUM*

Phase	Stability Range, °C	Space Lattice and Space Group	Unit Cell Dimensions, A	Atoms per Unit Cell	X-ray Density, g/cm³	Reference
α	Below ~ 115	Simple monoclinic $P2_1/m$	@ 21°C: a = 6.183 ± 0.001, b = 4.822 ± 0.001, c = 10.963 ± 0.001, β = 101.79° ± 0.01°	16	19.86	6
β	~115 - ~200	Body-centered monoclinic $I2/m$†	@190°C: a = 9.284 ± 0.003, b = 10.463 ± 0.004, c = 7.859 ± 0.003, β = 92.13° ± 0.03°	34	17.70	8
γ	~200 - 310	Face-centered orthohombic $Fddd$	@235°C: a = 3.159 ± 0.001, b = 5.768 ± 0.001, c = [illegible]	8	17.14	9
δ	310 - 452	Face-centered cubic $Fm3m$	@320°C: a = 4.6371 ± 0.0004	4	15.92	10
δ'	452 - 480	Body-centered tetragonal $I4/mmm$	@465°C: a = 3.34 ± 0.01, c = 4.44 ± 0.04	2	16.00	‡
ε	480 - 640	Body-centered cubic $Im3m$	@490°C: a = 3.6361 ± 0.0004	2	16.51	10

* From W. H. Zachariasen and F. H. Ellinger, Acta Cryst., 16: 780 (1963), W. H. Zachariasen and F. H. Ellinger, Acta Cryst., 16: 369 (1963), W. H. Zachariasen and F. H. Ellinger, Acta Cryst., 8: 431 (1955), and from F. H. Ellinger, AIME Transactions, 206: 1256 (1956).

† Although space group I2/m is not one of the "standard" space groups tabulated in the International Union of Crystallography, International Tables for X-ray Crystallography, Vol. 1, Kynock Press, Birmingham, England, 1952, its notation is retained to obtain a β-angle of approximately 90°.

‡ See Chapter 5.

- δ'–Pu is never observed by itself. Either the δ or ε phase is always present.
- The errors in determining structure are huge.
- The latent heat is essentially zero.
- The tetragonal distortion is tiny.

Table 3.11–HEATS OF TRANSITION OF THE PLUTONIUM ALLOTROPES.

	ΔH, cal/g-atom	ΔS, (cal/deg) /g-atom
α → β	900 ± 20	2.28
β → γ	160 ± 10	0.33
γ → δ	148 ± 15	0.25
δ → δ'	10 ± 10	0.01
δ' → ε	444 ± 10	0.59
ε → L	676 ± 10	0.74

3-2.3 *Specific Heats.* Specific heat data have also been reported[29, 31, 33] for the plutonium allotropes and liquid plutonium. Recently obtained values[33] are given in Table 3.12.

Sandenaw *et al*[34] and Sandenaw[35] reported results of

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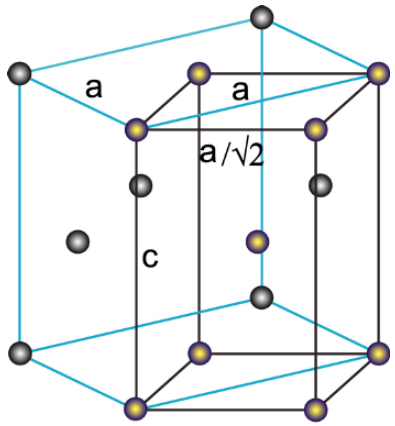
Pu as its own impurity (3)
δ'–is a strain-induced distortion leading to short-bonds.



fcc and bct representation

δ fcc 0.4637 nm
bct 0.4637 nm 0.328 nm ratio $\sqrt{2}$

δ' bct 0.444 nm 0.334 nm ratio 1.06x $\sqrt{2}$

ε bcc 0.36361 nm

δ-Pu is very soft (softer than Pb) and has an especially soft 110 shear mode.

The ratio c_{44} /c* =7 is the shear anisotropy. It is the largest for any fcc metal.

Poisson's ratio is about 0.43 along the soft direction, making Pu nearly like a liquid when squeezed in this direction.

δ' may just be a manifestation of strain field. But this is one easy route to short bonds in the fcc structure.

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What is suspect (1)
the Frenkel-pair picture of radiation damage in δ-plutonium

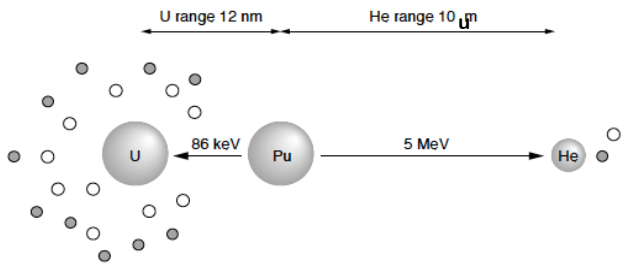
From LA Science, a string of assumptions based on assuming Pu is an ordinary fcc metal:

"assessment of radiation damage in gallium stabilized δ-phase plutonium by assuming it is a … "normal" face-centered-cubic (fcc) metal(s)… it has lattice defect properties consistent with those of other fcc metals such as nickel, copper, and austenitic stainless steels."

"To calculate the number of displacements, we need to know the so-called displacement energy, E_d, … not yet been measured, but …≅ 14 electron volts."

This is huge!! It takes about 100meV/atom to melt.

This yields, btw, 1 dpa=14.7 years based on cascading and questionable assumptions. dpa is not a useful number.



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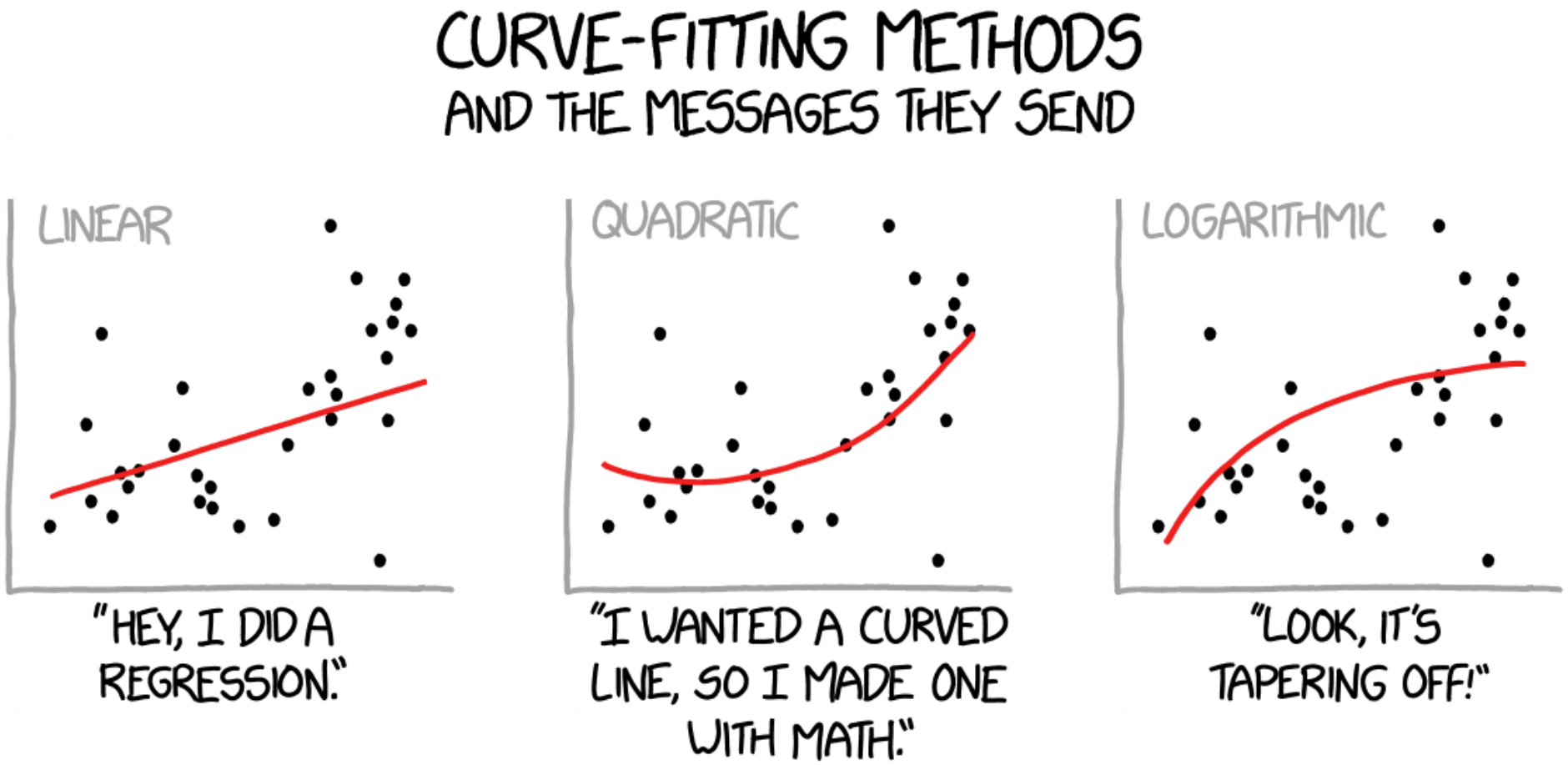
Before we get to the next bit…



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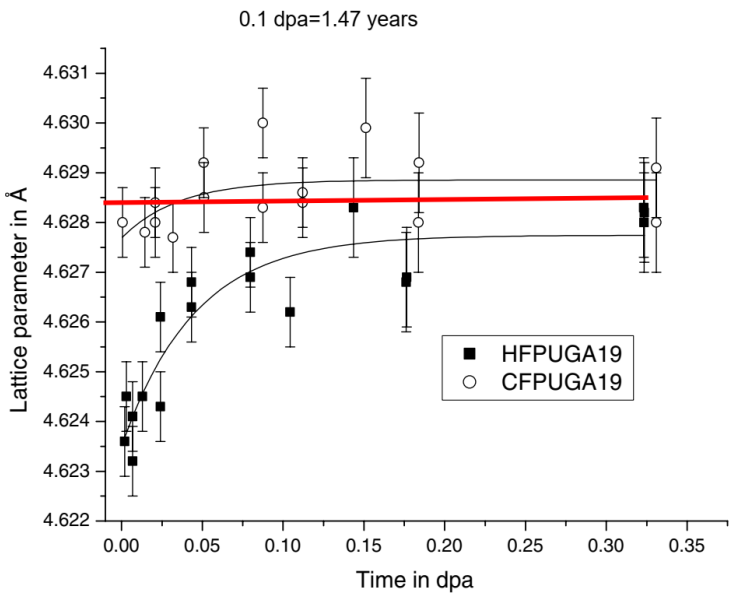
What is suspect (2)
diffraction studies do not show density decreases with age



B. Ravat [a,*], B. Oudot [a,b], N. Baclet [a]

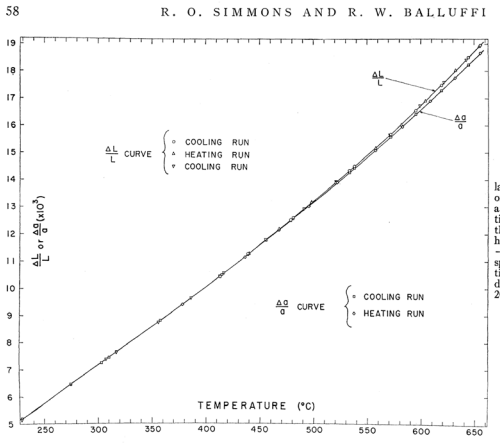


FIG. 3. Measured length and lattice parameter expansions of aluminum versus temperature. The fraction of additional atomic sites present in thermal equilibrium at the higher temperatures is $3(\Delta L/L - \Delta a/a)$. These sites correspond to the thermal generation of lattice-vacancy-type defects. $\Delta L/L = \Delta a/a = 0$ at 20°C.

Of the several sample of δ-plutonium used for this study, some had excessive Ga, some were not "homogenized".

The only result for a well-homogenized 2 at.% Ga sample (open circles) shows no change (my fit in red) in lattice parameter with time.

The lattice parameter is not useful for determining density in the presence of defects.

The difference between actual density and x-ray density is well studied and thermallpy activated.

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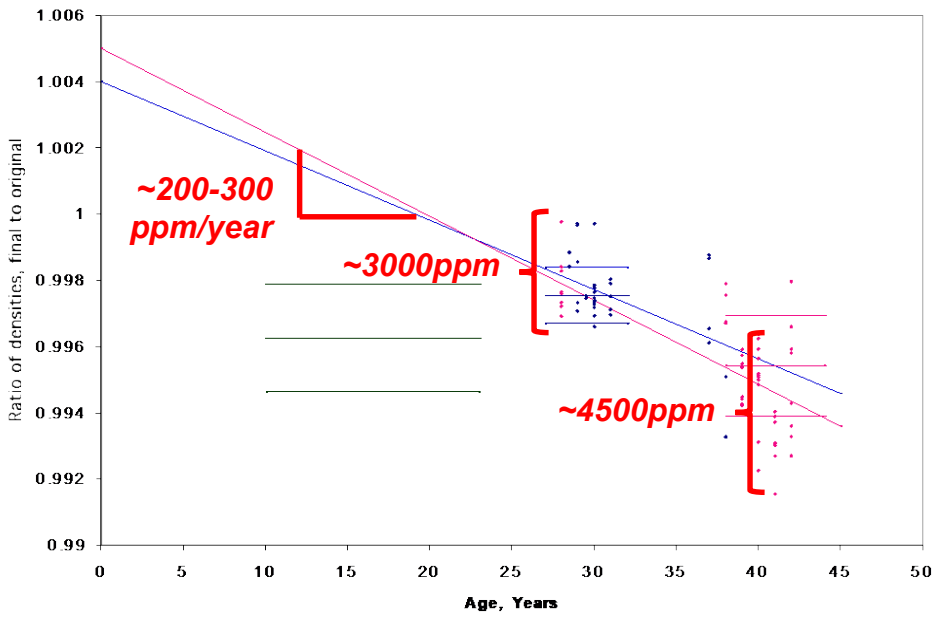
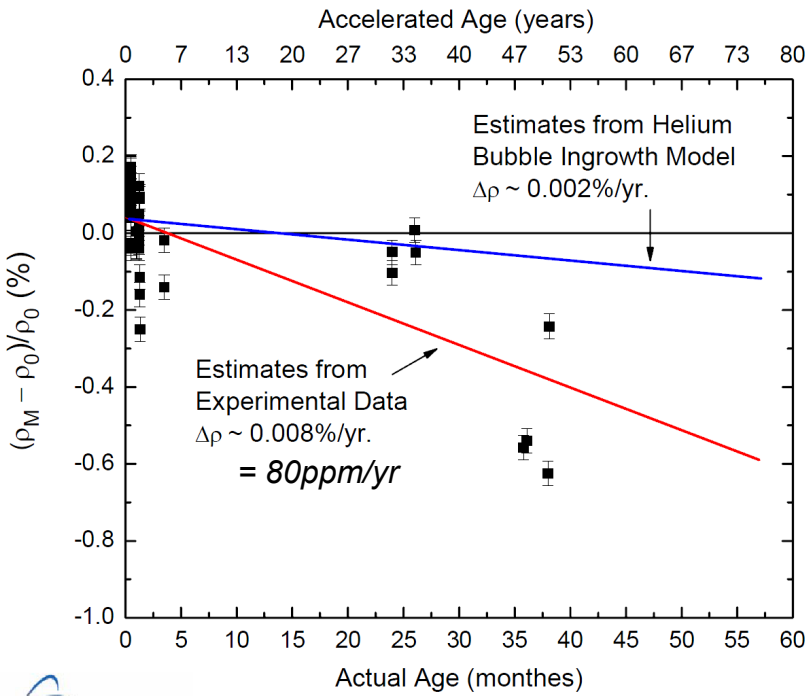
What is suspect (3)
density ands dilatometry studies do not show with any certainty that density decreases with age



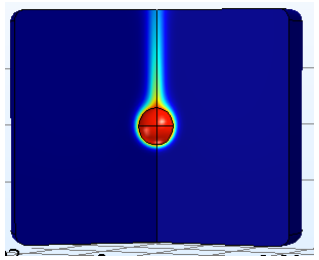


***210-270±70ppm/year**. (Mulford, 2002 LA-UR-02-1045)*
Robbie did the best she could but unknown systematic variations remain.

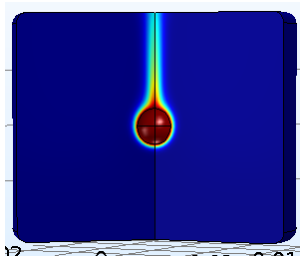
(Freibert, 2005 LA-UR-05-9007) too much scatter to be of use.

A missing systematic correction to immersion density measurements

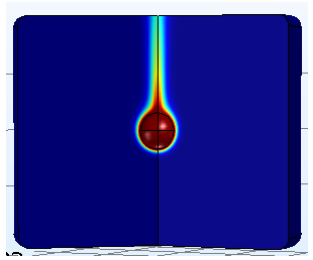
1.5mW/g



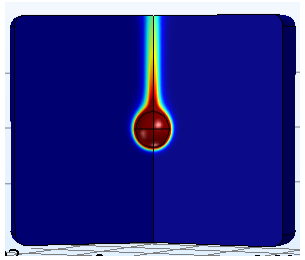
2 mW/g

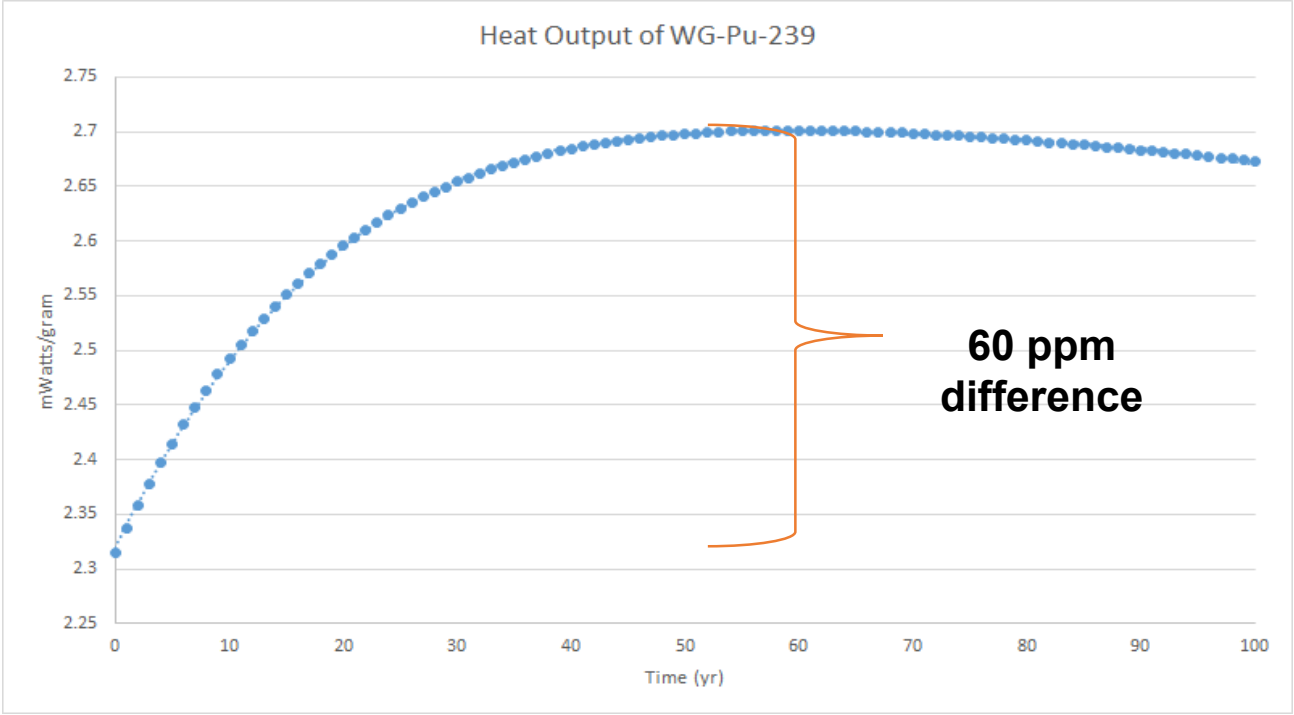


2.5mW/g



3 mW/g





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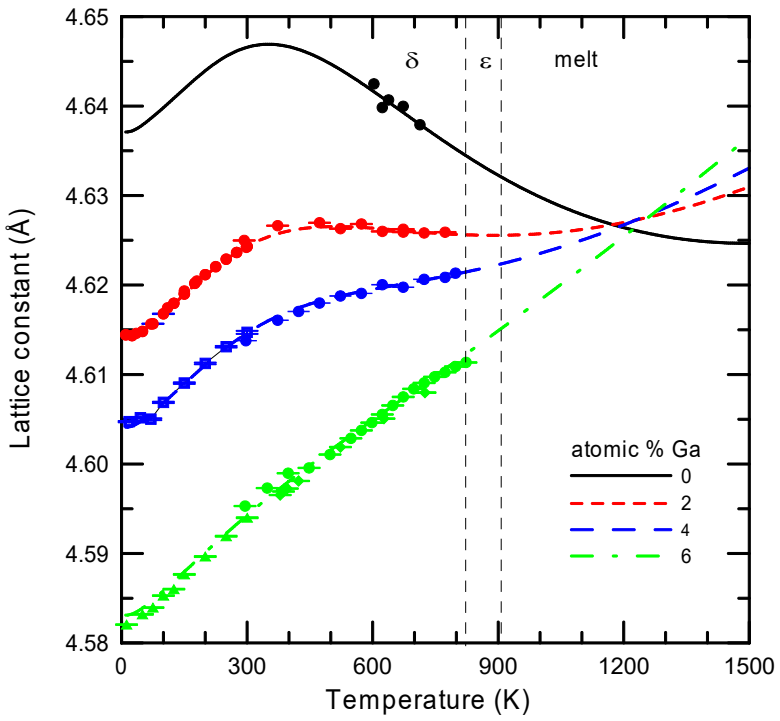
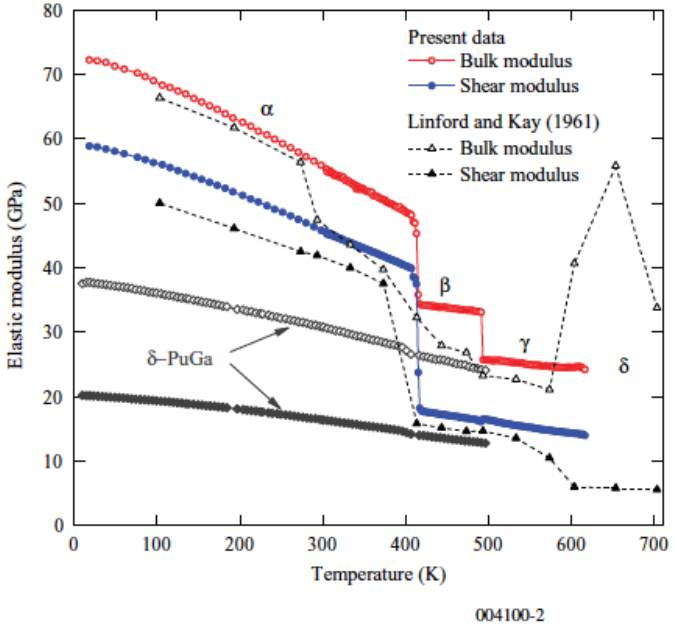
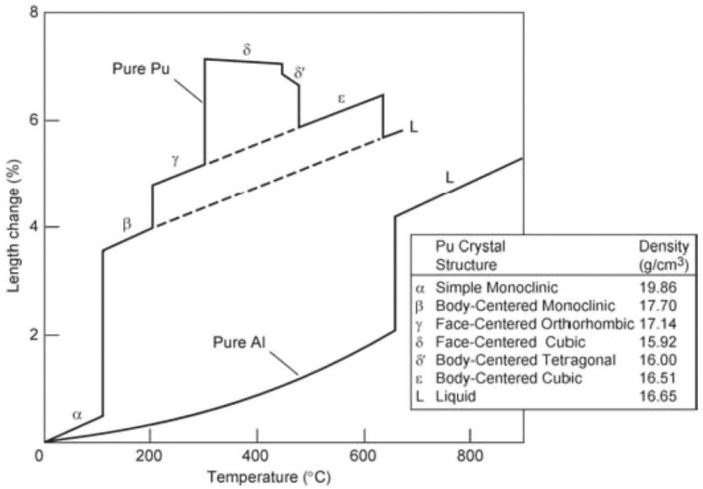
What we know (1)
Two thermodynamic properties are very unusual

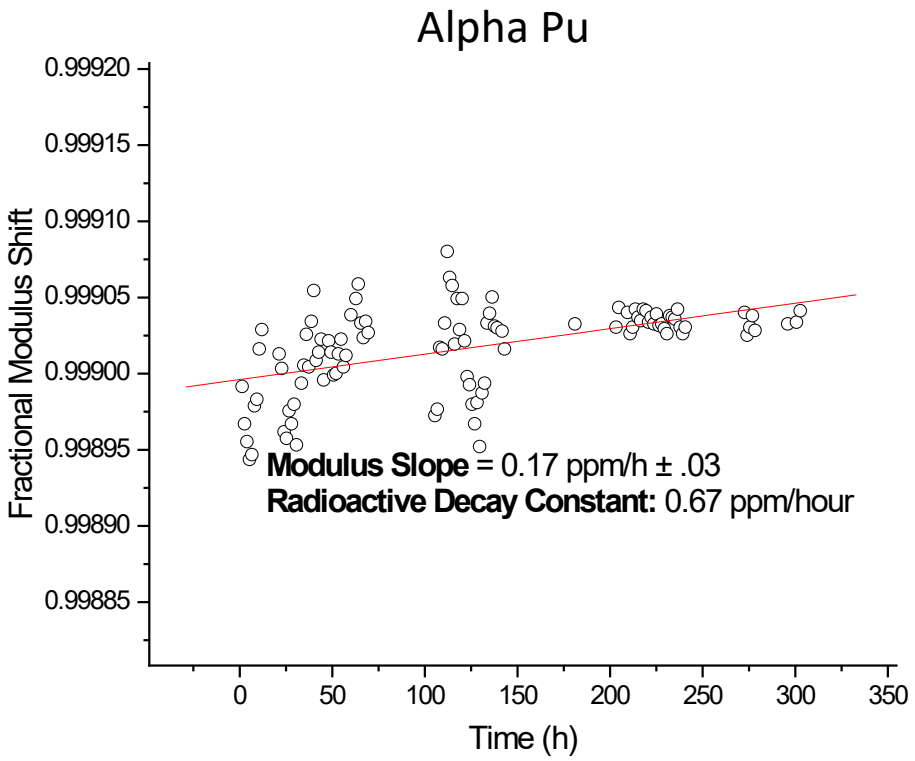


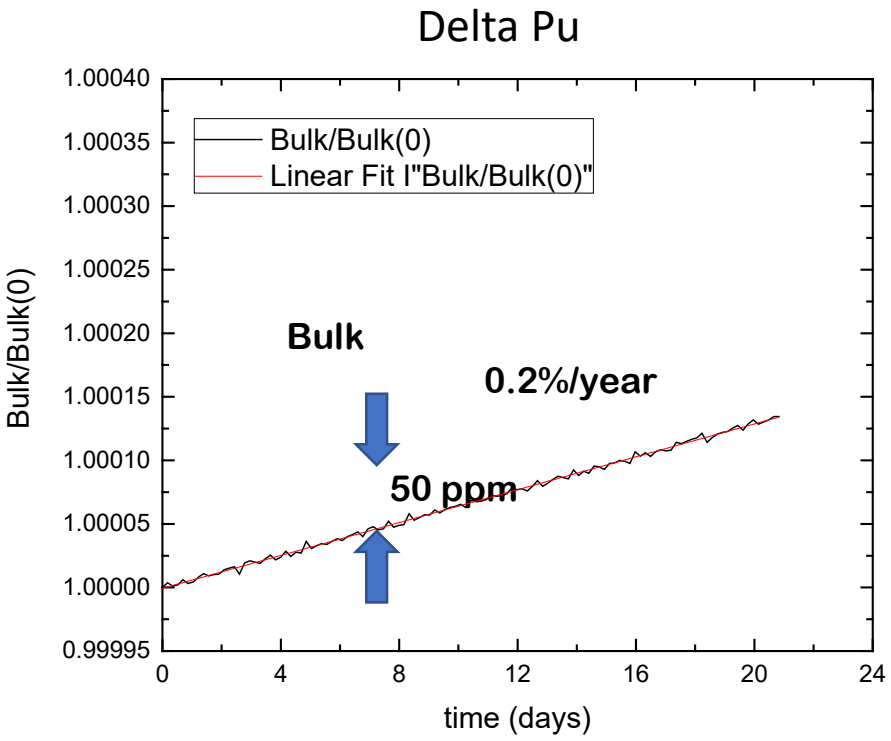


A. C. Lawson et al.



What we know (2)
The elastic moduli of both δ- and α- Pu increase with age at about the same rate





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What we know (3)

- Exponential decay factor for ^{239}Pu is 1.1×10^{12} s, or about 34,770 years.
- In one year, about 30 ppm of Pu is converted to U and He atoms.
- 85 keV of energy to the uranium, 5.2 Mev to the alpha, and a spectrum of mostly low energy gamma rays with the most probable at 51 keV.
- Most decay energy is converted immediately to heat, about 1.9 mW/g. Some energy remains trapped. It is that thermally-recoverable energy that we are trying to understand.
- Most of the alpha particle energy is deposited to electrons and then to heat: little local heating, 10μm-long track.
- Most of the U energy is deposited directly as heat.

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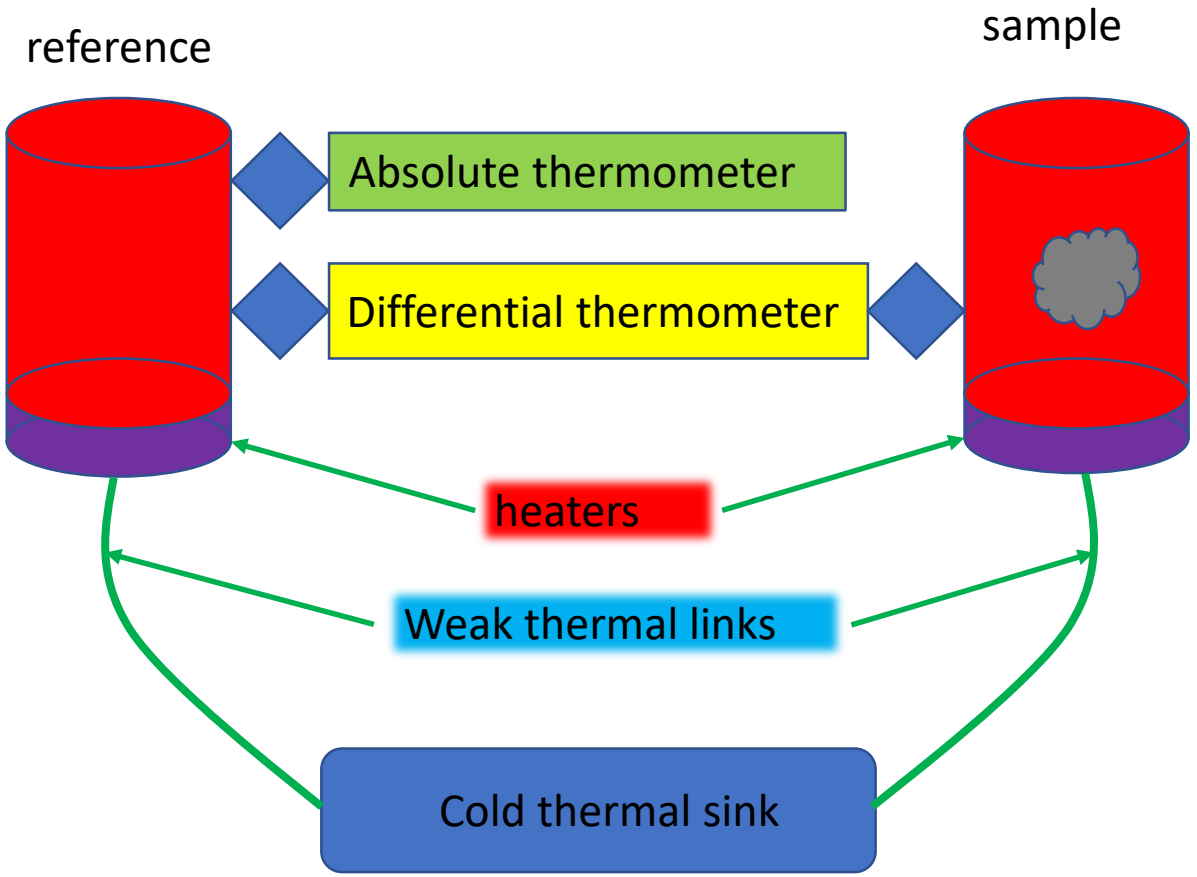
How differential scanning calorimetry works



Measures heat required to keep sample at same temperature as reference while reference temperature is increased at constant rate

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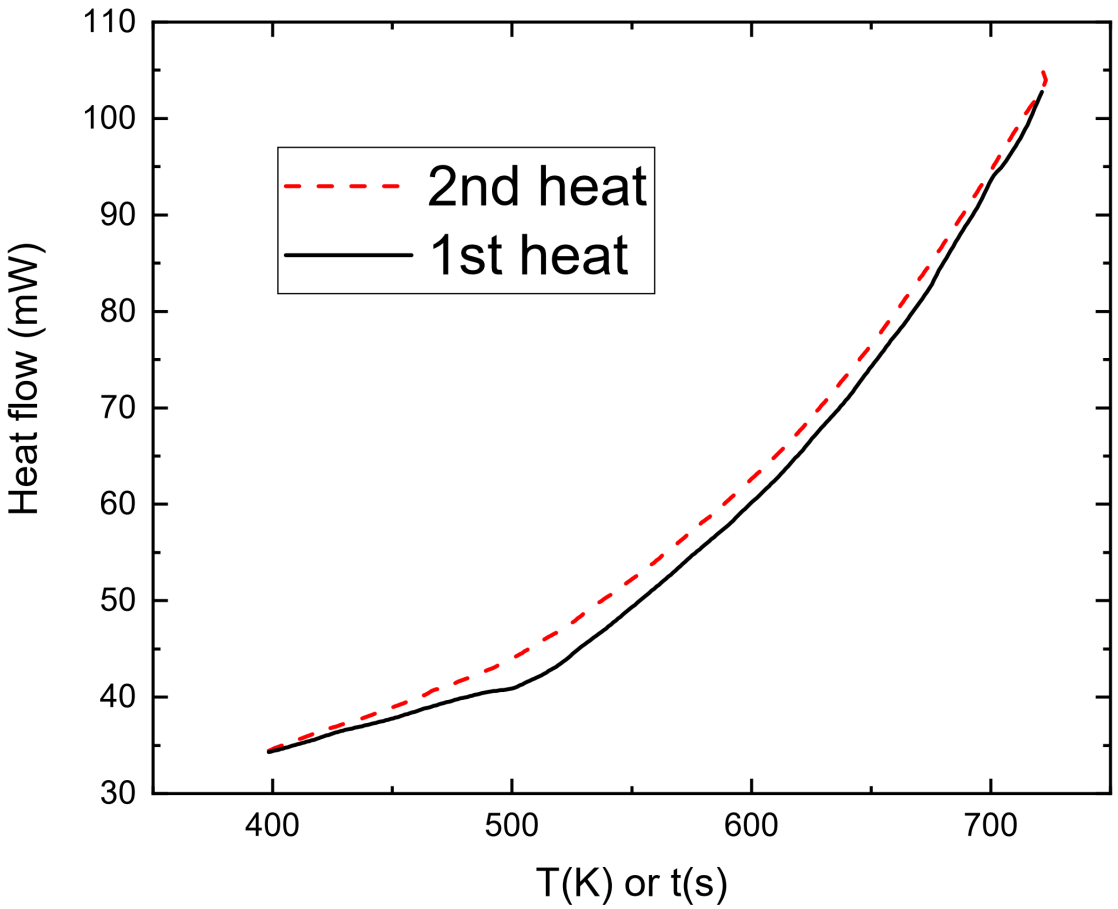
What we know (4)



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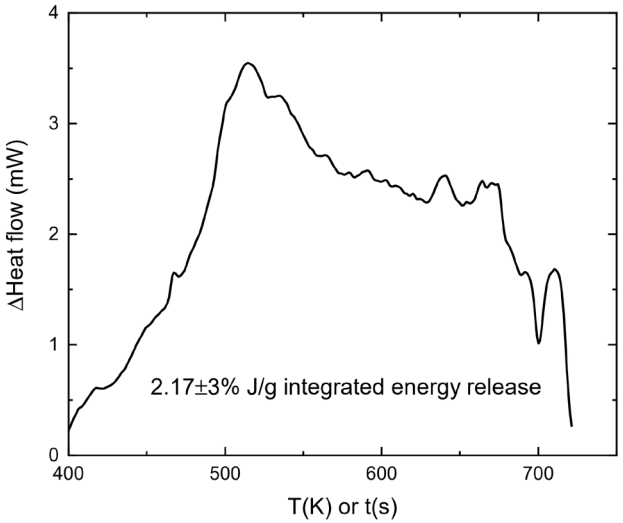
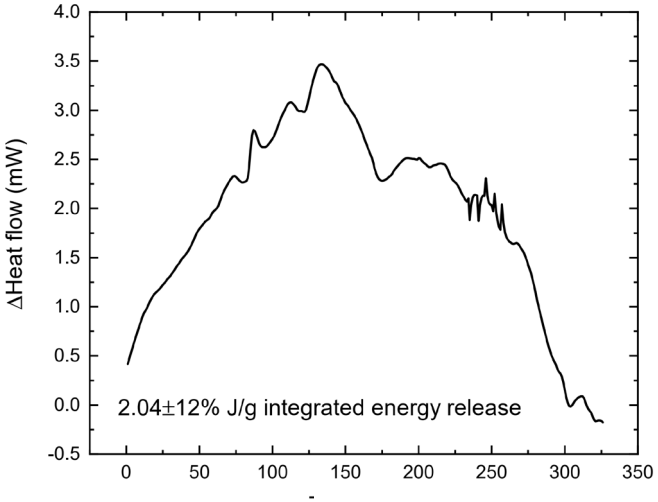
What we know (5)

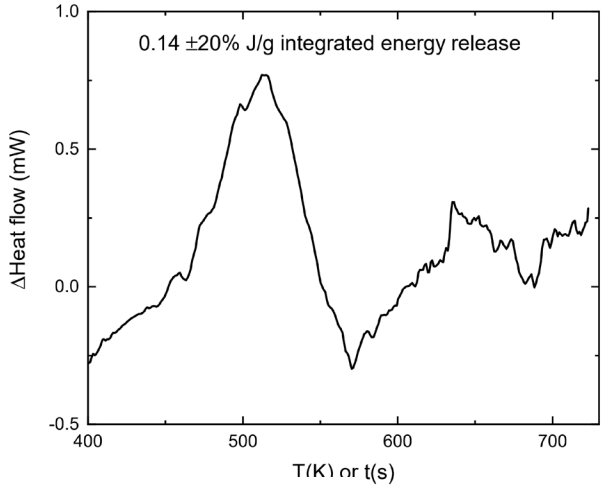
30 years

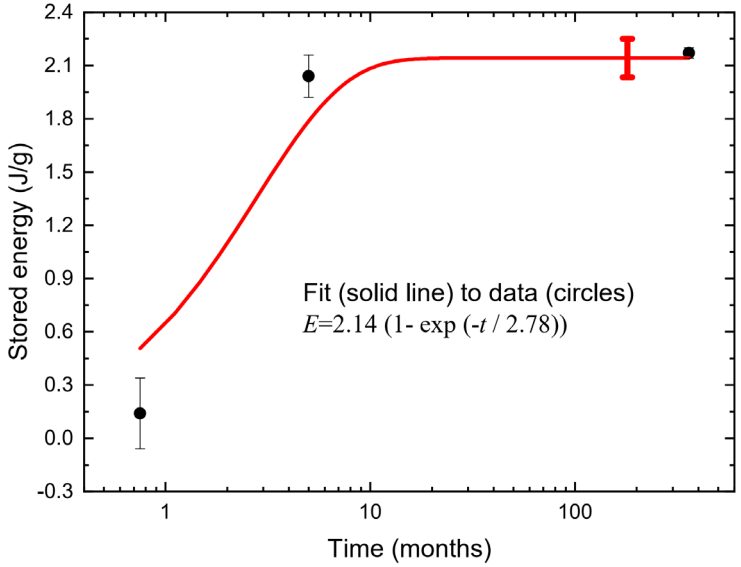


5 months



3 weeks





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α- Pu as δ- Pu with long-bond short-bond Pu impurities (1)

Neglecting duplicates we have:

- 12 long bond-short bond pairs using 24 atoms.
- 17 long bonds.
- Thus about 60% of the unit cell is long bond-short-bond pairs.

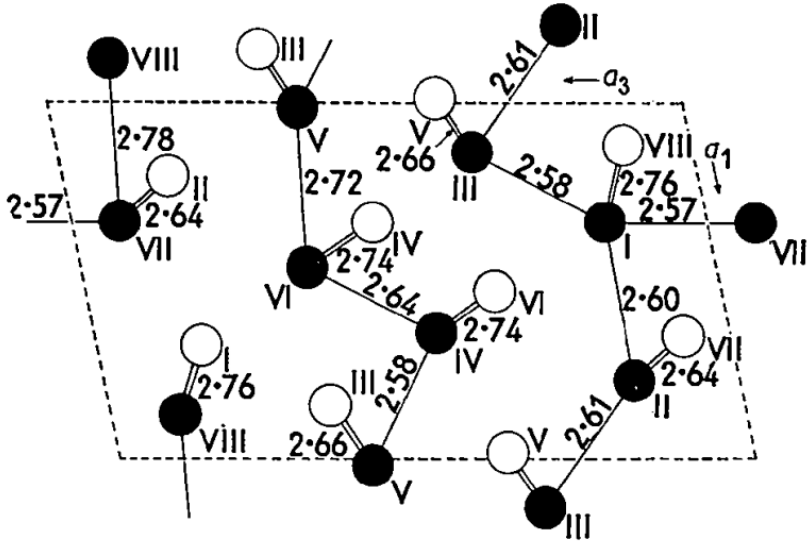

Fig. 3. Projection of the structure on the (010) plane. Filled circles represent atoms at $y = \frac{1}{4}$, open circles atoms at $y = -\frac{1}{4}$. Only the short bonds are indicated in the projection.

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α- Pu as δ- Pu with long-bond short-bond Pu impurities (2)

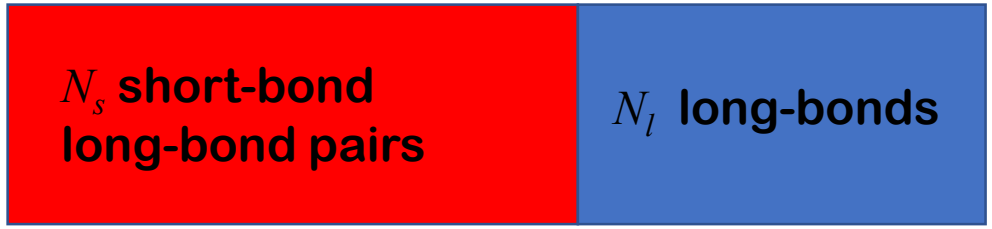
How can radiation damage induce bond defects and what do they do?

- **From decay flash heating, regions of about 100nm radius must produce pressure pulses from thermal expansion, just what is needed to compress the alloy toward the α-phase, destabilizing locally δ-Pu.**
- **Such an effect can also change locally an δ-Pu specimen by creating excess short bonds.**
- **Both the U and the flash heating can produce short bonds, so that two time scales are expected.**
- **50 J/g (100 meV/atom) takes Pu from ambient temperature to melt.**
- **The energy is deposited locally, so each decay can raise 10^6 Pu atoms above melt.**
- **In about 20 days, the U recoil deposits 50J/g, raising all the atoms, more or less, above melt. This is the DSC time scale.**

Effects of radiation damage in δ- Pu (1)

Considering the as an impurity, we can find what the bulk modulus B of the impurity must be to make adding that impurity to δ- Pu into δ- Pu by making the pressure everywhere the same for a small volume change dV.

$$B_a \frac{dV}{N_l + N_s} = B_d \frac{dV_d}{N_l} = B_s \frac{dV_s}{N_s}$$



$$B_s = 110\ GPa$$

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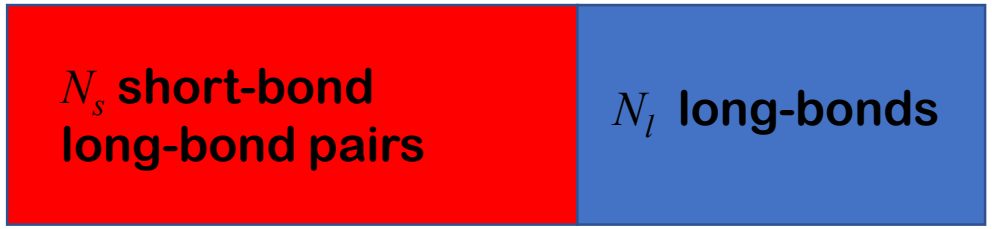
Effects of radiation damage in δ- Pu (2)

We do the same for the density of the short-bond long-bond pairs:

$$\rho_a = (\rho_d * N_l + \rho_s * N_s)/(N_l + N_s)$$

$$\rho_s = 22 \text{ g/cc.}$$



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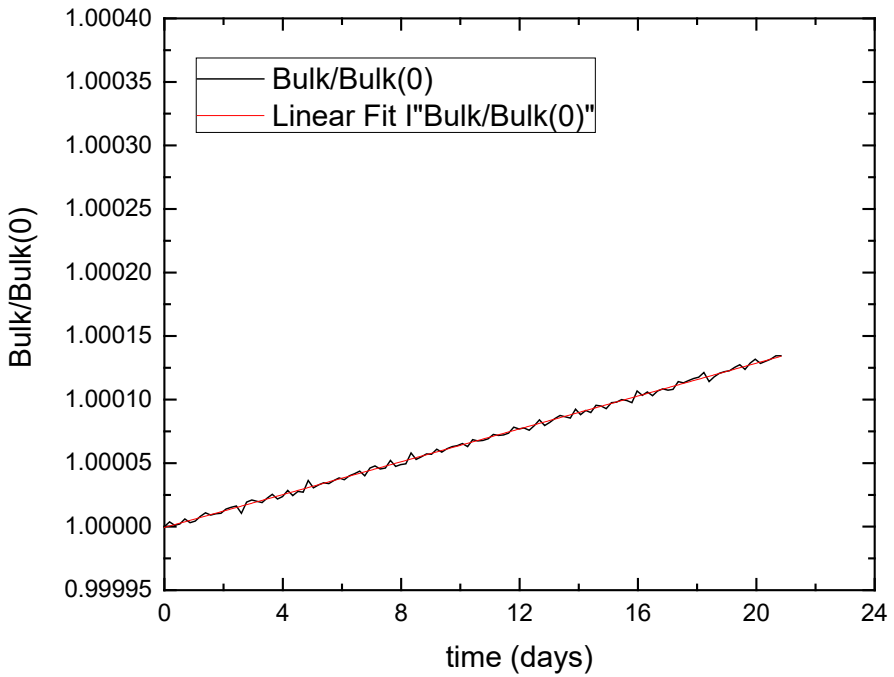
Effects of radiation damage in δ- Pu (3)

- We know from DSC study that at 8 years, all the thermally-recoverable effects of damage have saturated.
- The only quantity linear at 8 years is the rate of decay product production (U or He) of 30 ppm/yr.
- We know the bulk modulus of the short-bond long-bond pairs and so we know how many must be produced per U to get the RUS results (0.2%/yr or 2000 ppm/year).
- Thus about 50 short-bond long-bond pairs per decay are retained.
- This yields a density increase of about 600 ppm/yr opposite current thinking.



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Effects of radiation damage in δ- Pu (4)

We still do not know the number of defects per decay produced by the U recoil flash heating:

- **It is tempting to use the activation energy of the RUS slope and assign it to the defect energy but too many things are going on at once:**
  - **Ga diffusion.**
  - **Thermal production of defects.**
  - **Self-annealing.**

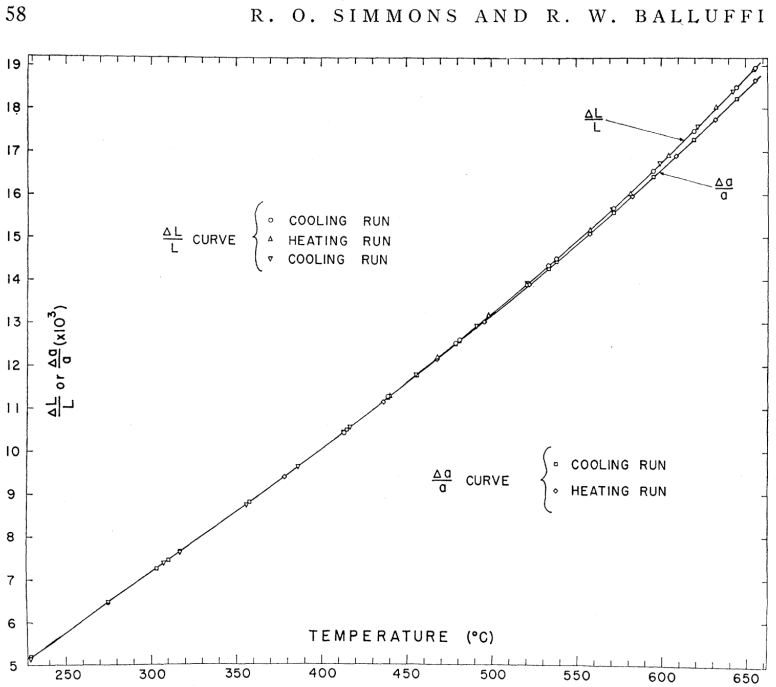

FIG. 3. Measured length and lattice parameter expansions of aluminum *versus* temperature. The fraction of additional atomic sites present in thermal equilibrium at the higher temperatures is 3 $(\Delta L/L - \Delta a/a)$. These sites correspond to the thermal generation of lattice-vacancy-type defects. $\Delta L/L = \Delta a/a = 0$ at 20°C.

Effects of radiation damage in δ- Pu (5)

How can we determine the number of defects per decay or equivalently, the energy per defect, that produce the DSC results?

- It is tempting to use DFT supercell calculations but the unit cell volume for those calculations is fixed so calculations of the (testable) change in bulk modulus cannot be obtained.

- But we do know the total energy stored from DSC. So:
  - If we can see the DSC time scale in RUS measurements of freshly-prepared material, because we know how many defects produce a given change in bulk modulus, and the total energy, we get the number.

  - If we can see the DSC time scale in dilatometer measurements of freshly-prepared material, because we know how many defects produce a given change in density, and the total energy, we get the number.

- Can we use the diffuse background in diffraction, pdf, or EXAFS to see the DSC time scale and get the number that way? Hard to do.

- Can we correct historical data for thermal buoyancy?

Effects of radiation damage in δ- Pu (6)

Implications:

- If we confirm our predictions then we know the size we compute for defects is correct.
- We know that the thermally-recoverable defects saturate in a few months.
- The 30 ppm/yr of U production will after many months, produce about 2000 ppm/yr of defect clusters and so they should start to overlap at about 500 years.
- But Americium etc. tend to make short bonds less stable so this will start to reduce the stiffening and densification effects after a few decades.
- Although the Pu is stiffening, it is also densifying, so there is pre-compression of plutonium as it ages,

We have not succeeded in answering all of our questions. Indeed, we sometimes feel that we have not completely answered any of them. The answers we have found only served to raise a whole new set of questions. In some ways we feel that we are as confused as ever, but we think we are now confused on a higher level, and about more important things.

-Author unknown