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Elastic Moduli of Unalloyed Delta Plutonium

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Los Alamos National Laboratory

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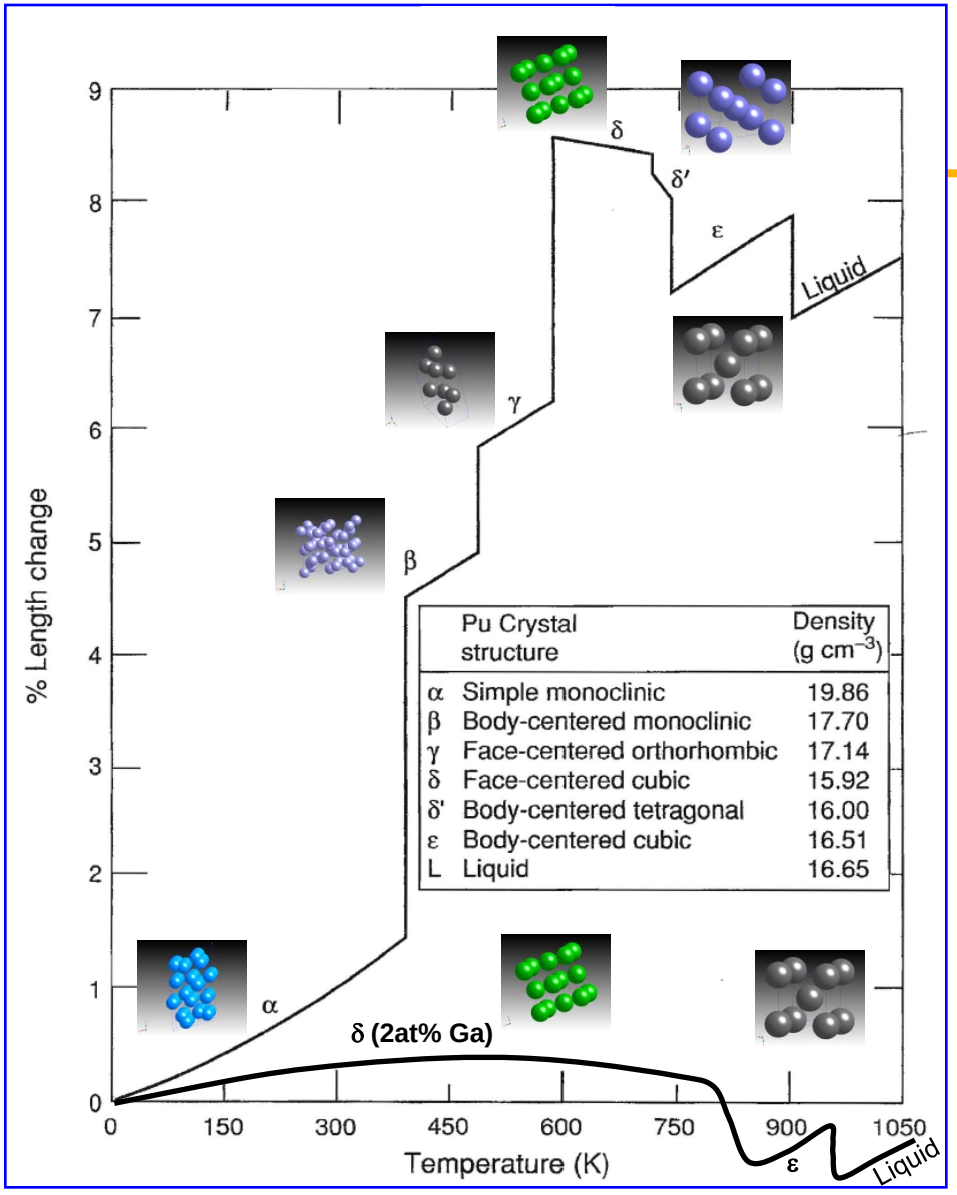


Plutonium: An Inherently Unstable Element

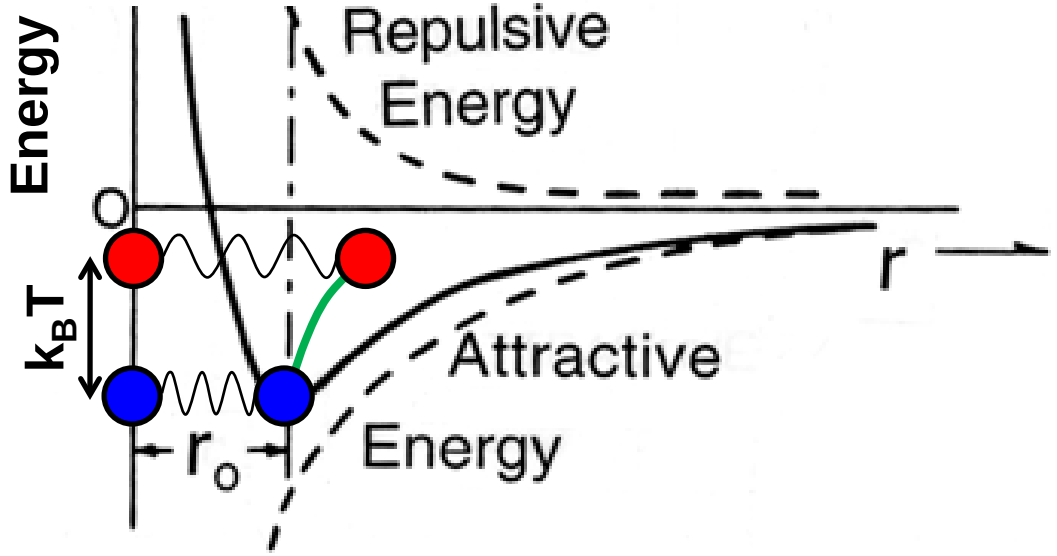
- **Phase Transformations**
  - 5 Solid-Solid Allotropic Transformations
  - Shear and Diffusion Driven
- **Thermodynamics**
  - Quantitative and Qualitative Character
- **Kinetics (Heating vs. Cooling)**
  - Rapid vs. Sluggish Atomic Movements
- **Ga as an Impurity**
  - Interstitial (Lattice Const. increase: α')
- **Ga Alloying**
  - Lowers δ-Pu Phase Free Energy and Stabilizes δ-Pu
  - Substitutional in δ-Pu (XAFS)
  - Alters Electronic Structure (TEC - → +)
  - Diffusional δ↔ε transformation
- **Impact of Microstructure and Impurities**
  - Grain size, Morphology, and Texture
  - Pu_6Fe and other Inclusions

Fundamental Bulk Solid Thermodynamics: Interatomic Potential and Thermodynamic Properties

Interatomic Potential Drives:

- **Phase Transformations**
- **Thermodynamics**
- **Kinetics (Heating vs. Cooling)**
- **Ga as an Impurity**
- **Ga Alloying**
- **Impact on Microstructure and Impurity Acquisition**
- **Anharmonic Effects**

Φ(r) Pair Potential Energy



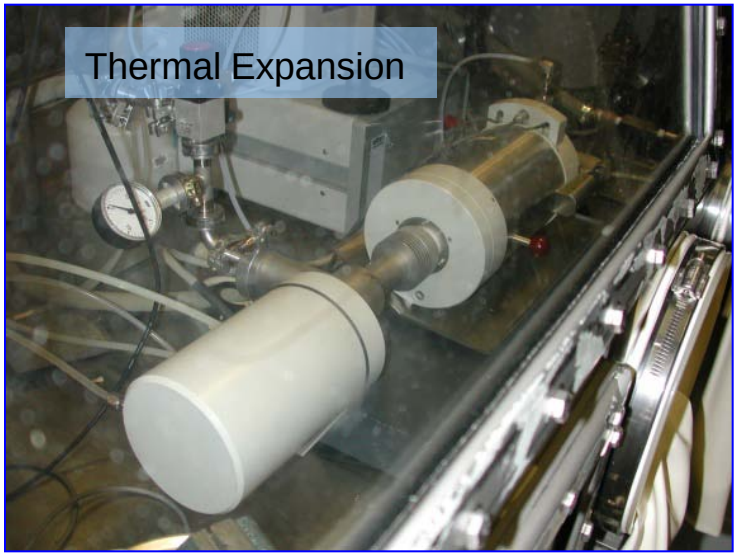
Bulk Modulus: $$B = \frac{2}{3r_o}\frac{\partial^2 \Phi(r)}{\partial^2 r}$$

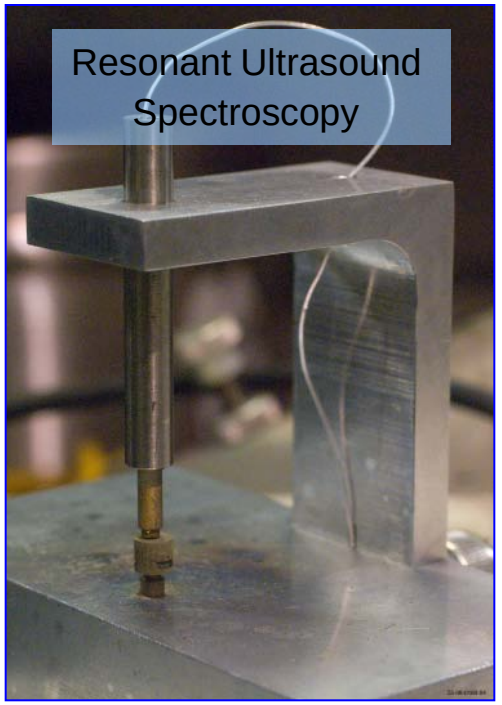
Linear Thermal Expansion: $$\alpha = \frac{1}{L_o}\frac{\partial L}{\partial T};\ L_o \approx {r_o N_A}/{3}$$

Thermophysical Properties: Density, Thermal Expansion and Resonant Ultrasound Spectrometry

The following body of work is explicitly dependent on the coupling of the thermophysical properties of density, thermal expansion and elastic moduli.

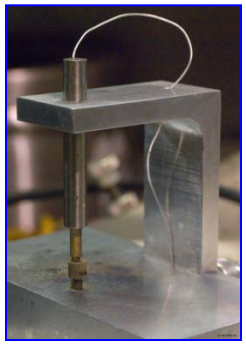
ρ_{To} → $\frac{\Delta L(T)}{L_{To}} \approx -\frac{\Delta \rho(T)}{3\rho_{To}}$ → $B(\rho(T), \upsilon_L, \upsilon_T)$ and $G(\rho, \upsilon_T)$

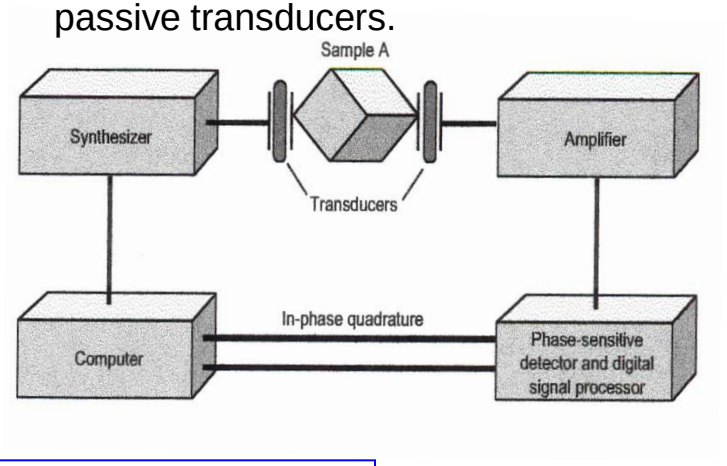




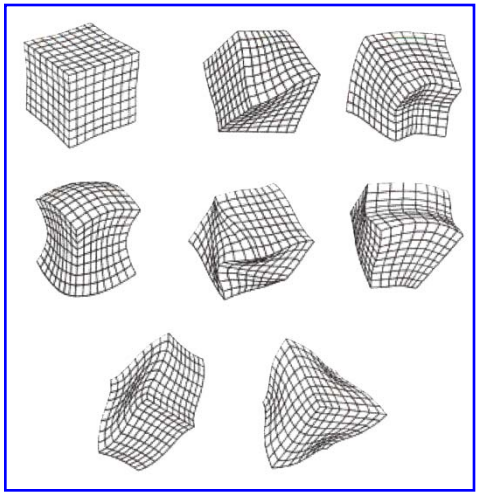
Resonant Ultrasound Spectrometry

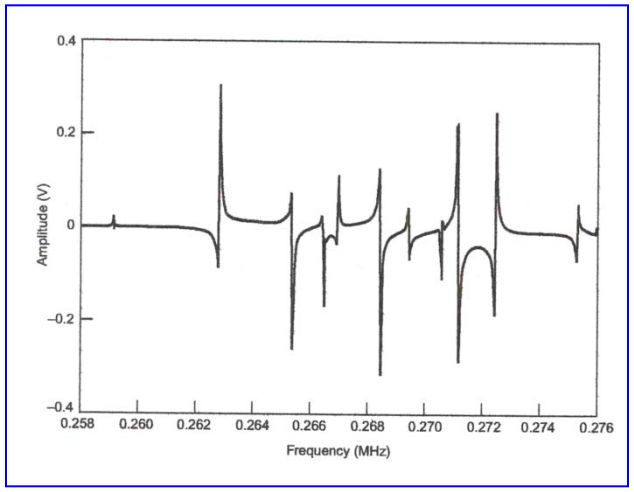
Samples are mounted between acoustic active and passive transducers.



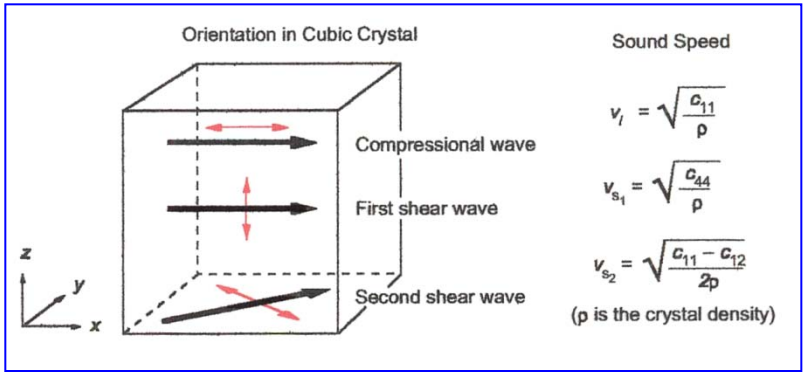


When driven acoustically to resonance, the samples vibrate in standing modes unique to the resonant frequency.



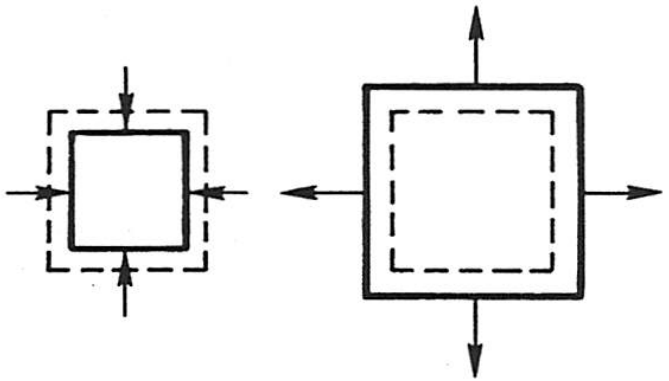


The response spectrum is dependent on geometry, density and elastic moduli. The moduli are determined by solving the inverse problem - the elastic response of an ideal elastic solid of identical geometry and density and crystalline structure.

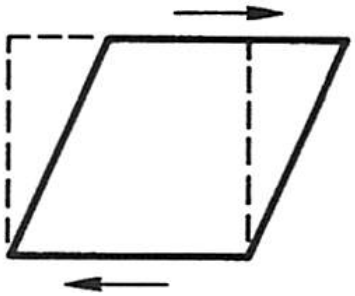


Elastic Moduli and Associated Mechanical Deformations

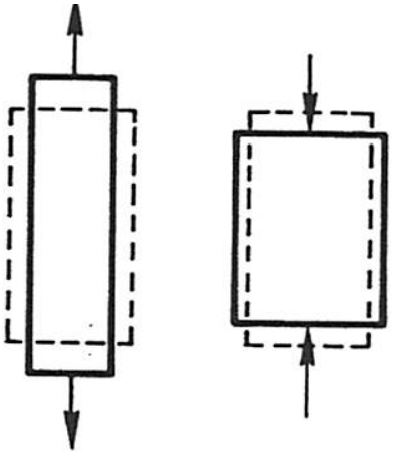
Bulk Modulus = B
Compressibility =1/B



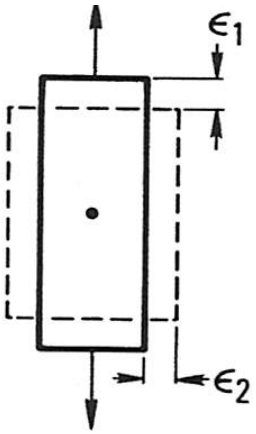
Shear Modulus = G



Young's Modulus = E



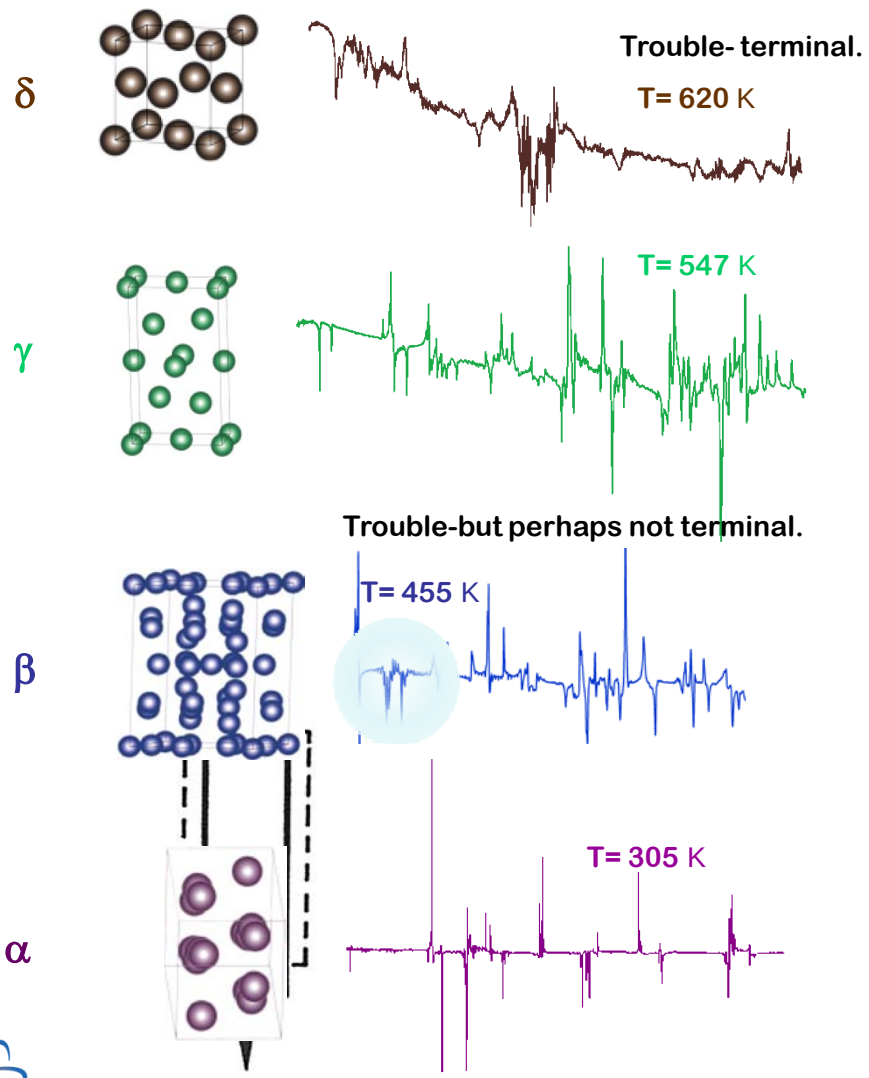
Poisson's Ratio = υ



Elastic Properties Compendium for Pu and Pu-Ga alloys

Sample	c_{11} (GPa)	Bulk(GPa)	Shear (GPa)	Density (gm/cc)
single crystal δ–Pu 3.3 at.% Ga new (Ledbetter and Moment)	51.40	29.90	16.20	
polycrystal δ–Pu 2.36 at. % Ga new	52.3±0.15	30.60	16.30	15.47
polycrystal δ–Pu 3.30 at. % Ga new 297K	51.8±0.44	29.60	16.68	15.70
polycrystal δ–Pu 3.30 at. % Ga 2 year 292K Homog.	52.7±0.62	30.50	16.67	15.70
polycrystal δ–Pu 3.30 at. % Ga 1.5 year 298K	51.8±0.55	29.40	16.79	15.70
polycrystal δ–Pu 4.64 at. % Ga new	53.30	30.70	16.98	15.59
polycrystal δ–Pu 4.64 at. % Ga new	53.90	31.30	16.98	15.59
polycrystal δ–Pu 4.64 at. % Ga 9 months ~298K	53.90		16.98	15.59
polycrystal δ–Pu 4.64 at. % Ga 11months 295.87K	54.10		16.96	15.59
polycrystal δ–Pu 4.64 at. % Ga 11months 275.41K	55.05		17.27	15.59
polycrystal δ–Pu 1.73 at. % Ga 15y	47.50	26.70	15.60	15.70
polycrystal δ–Pu 3.902 at. % Ga 15y	58.40	34.30	18.10	15.51
polycrystal δ–Pu 5.53 at. % Ga 44y	50.00	27.00	17.20	15.48
polycrystal δ–Pu242 5.5 at. % Al 1.5 year 298K	51.28	27.90	17.51	15.74
cast α-Pu (Laquer)	104.60	46.60	43.50	
cast α-Pu (new) 297K	112.80	54.40	43.70	19.70
AAP measured 13 Aug 2002 (0.4 dpa)	51.30	29.70	16.20	15.69

High Temperature Elastic Moduli Measurements



RUS for High temp. Pu polycrystal measurements:

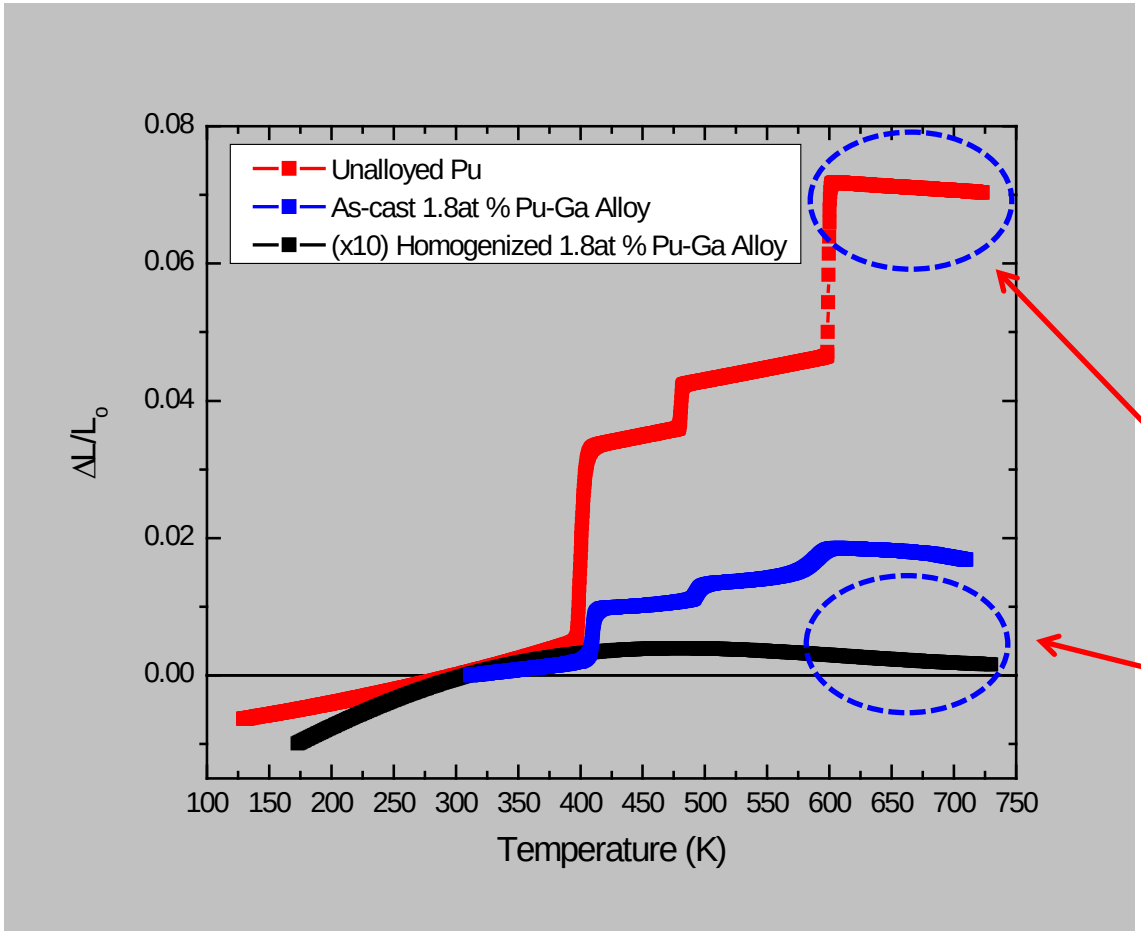
- all metal/ceramic system to survive months near a strong alpha emitter.
- ^{4}He around Pu for T < 300K.
- vacuum around Pu for T > 300K.

High temperature range:

- 300K-700K; stability 1mK.
- spans α, β, γ phases and into δ

This is an early model. With redesign, this system has much improved performance.

Thermal Expansion of Unalloyed δ-Pu and 2at% Ga Stabilized δ-Pu



For many years, it has been recognized that unalloyed δ-Pu and 2at% Ga stabilized δ-Pu exhibited a similar thermal expansion behavior in the same temperature range.

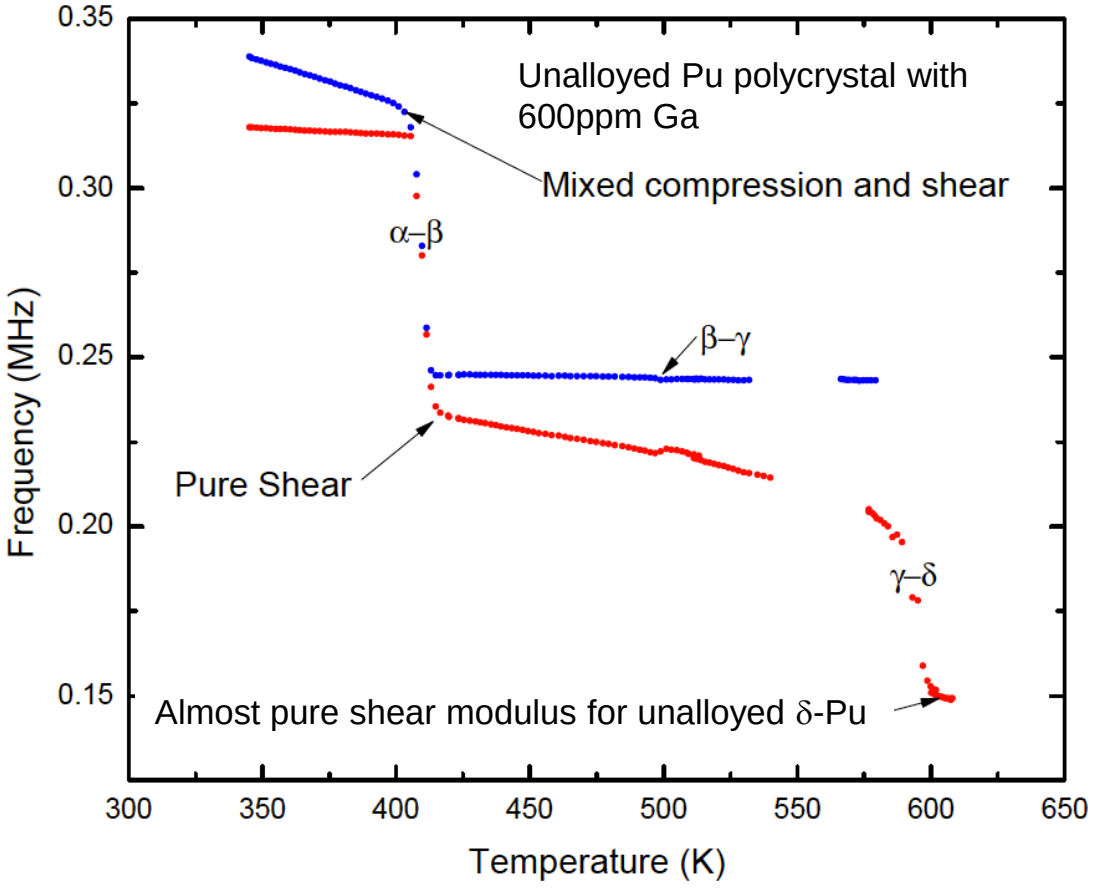
$\alpha_{\delta\text{-Pu}} = -1.3 \times 10^{-5}\ C^{o-1}$

$\alpha_{\delta\text{-PuGa}} = -2 \times 10^{-6}\ C^{o-1}$

But what about the elastic moduli in this temperature range?

Elastic Behavior of Low Defect/High Density Unalloyed Pu Materials

Shear and bulk modulus exhibit unalloyed phase transformations, but transformations are broadened.



Materials production affects experimental results.

Unalloyed Pu castings undergo >24% volume reduction from liquid to RT solid inducing microcracking and defects.

Metallurgical and casting "tricks" get you close to α-Pu (19.86g/cc), but not quite
(1) Ga microalloying (~600ppm)
(2) Puck casting (surface stress relief);
(3) Thermal cycling
($CTE_{\alpha\text{-}Pu} > CTE_{\beta\text{-}Pu}$)

Metallurgical tricks allow us to approach α-Pu, but Ga (as do other impurities) impact the phase transformation character and kinetics.

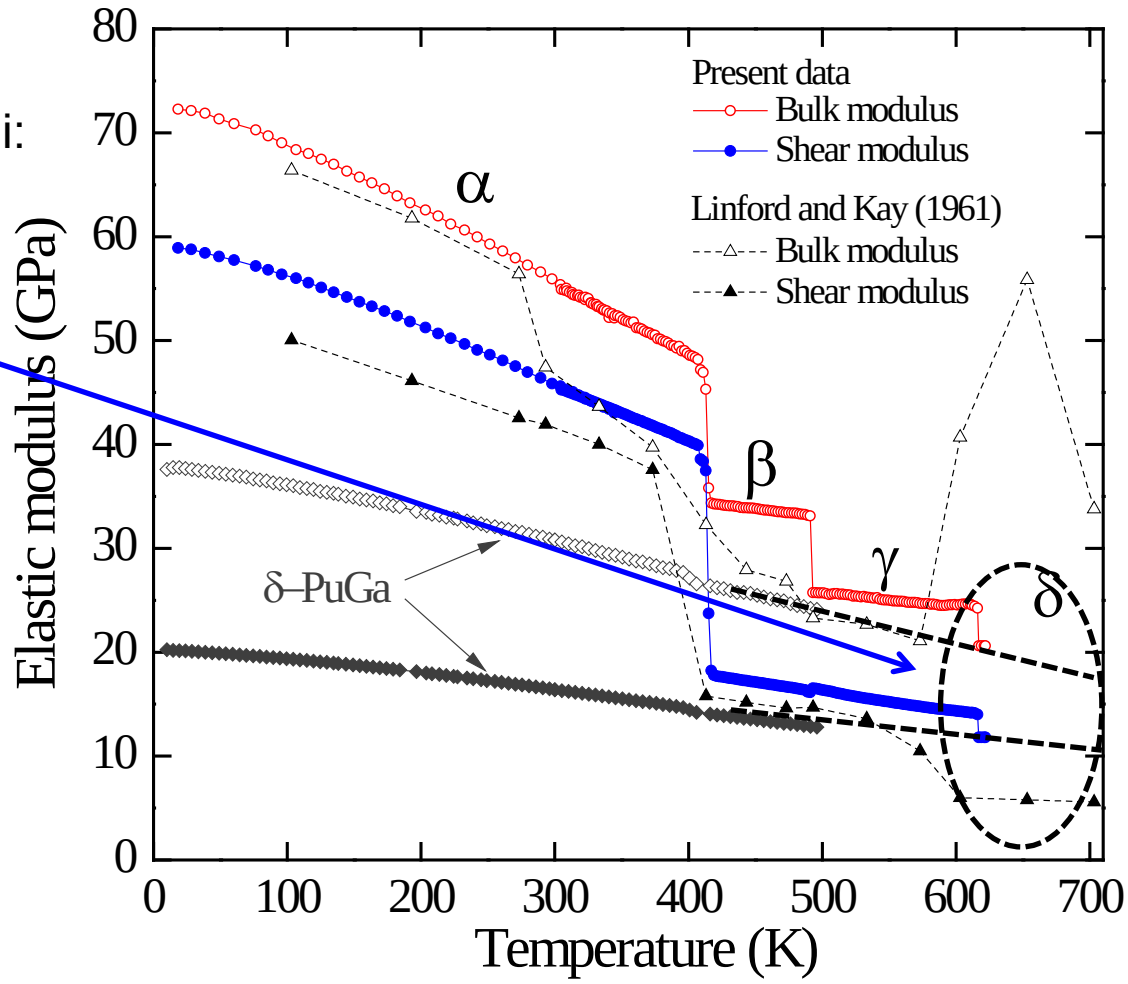
Unalloyed δ-Pu and 2at% Ga stabilized δ-Pu are elastically similar!

- Unalloyed and Ga alloyed δ-Pu exhibit same values of bulk and shear elastic moduli:

$$B_{\delta-Pu} = 20.6\ \text{GPa}$$
$$G_{\delta-Pu} = 11.8\ \text{GPa}$$
$$B^{Ext.}_{\delta-PuGa} = 22\ \text{GPa}$$
$$G^{Ext.}_{\delta-PuGa} = 12\ \text{GPa}$$

- α→β, β→γ, and γ→δ Pu transformation are continuous.

- β-Pu and γ-Pu exhibit the same shear modulus with a 30% variation in bulk modulus.

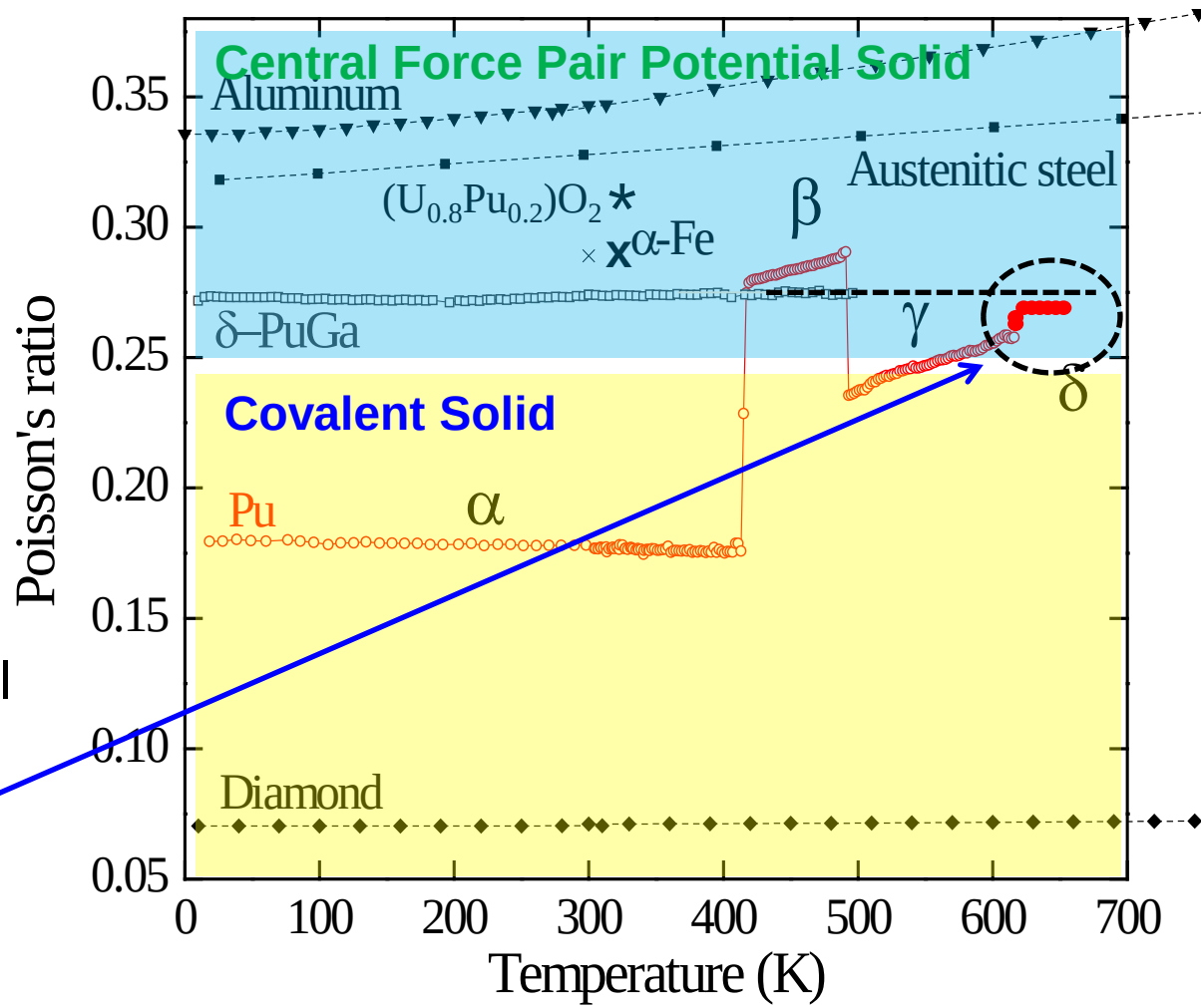


Poisson's Ratio of Ga Alloyed and Unalloyed Pu

- α-Pu exhibits Poisson ratio similar to a covalent solid.
- Although β-Pu and γ-Pu exhibit the same shear modulus, Poisson's ratio is 20% different.
- Unalloyed δ-Pu and Ga stabilized δ-Pu shows central force pair potential behavior typical of other FCC metals.

$\nu_{\delta\text{-Pu}} = 0.27$

$\nu_{\delta\text{-PuGa}} = 0.28$

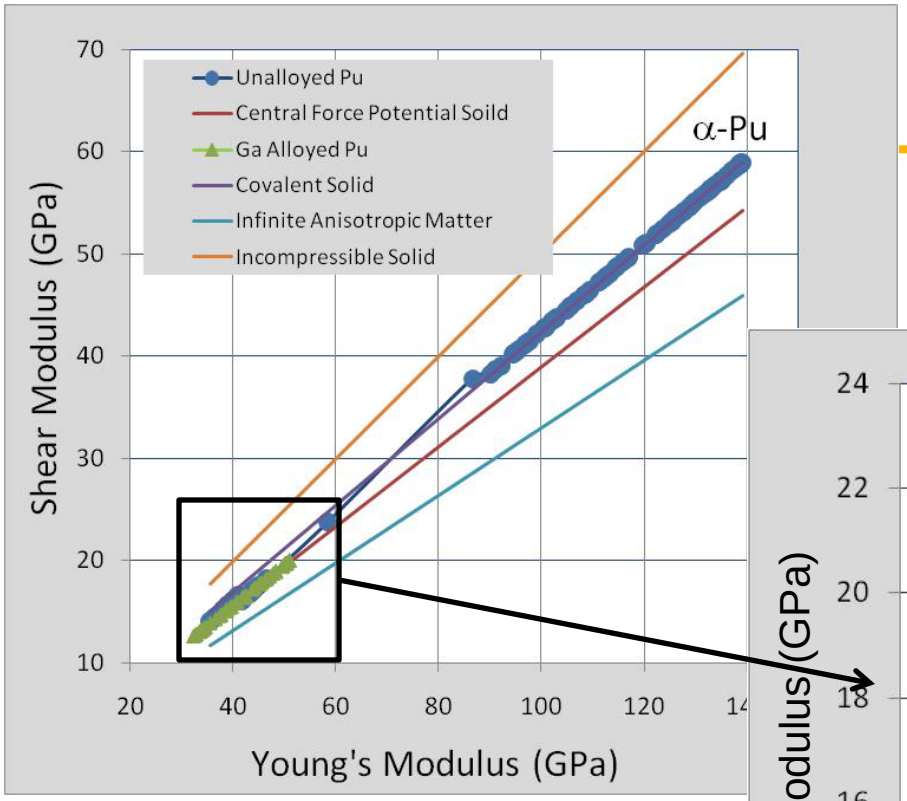


Interatomic Bonding in Plutonium

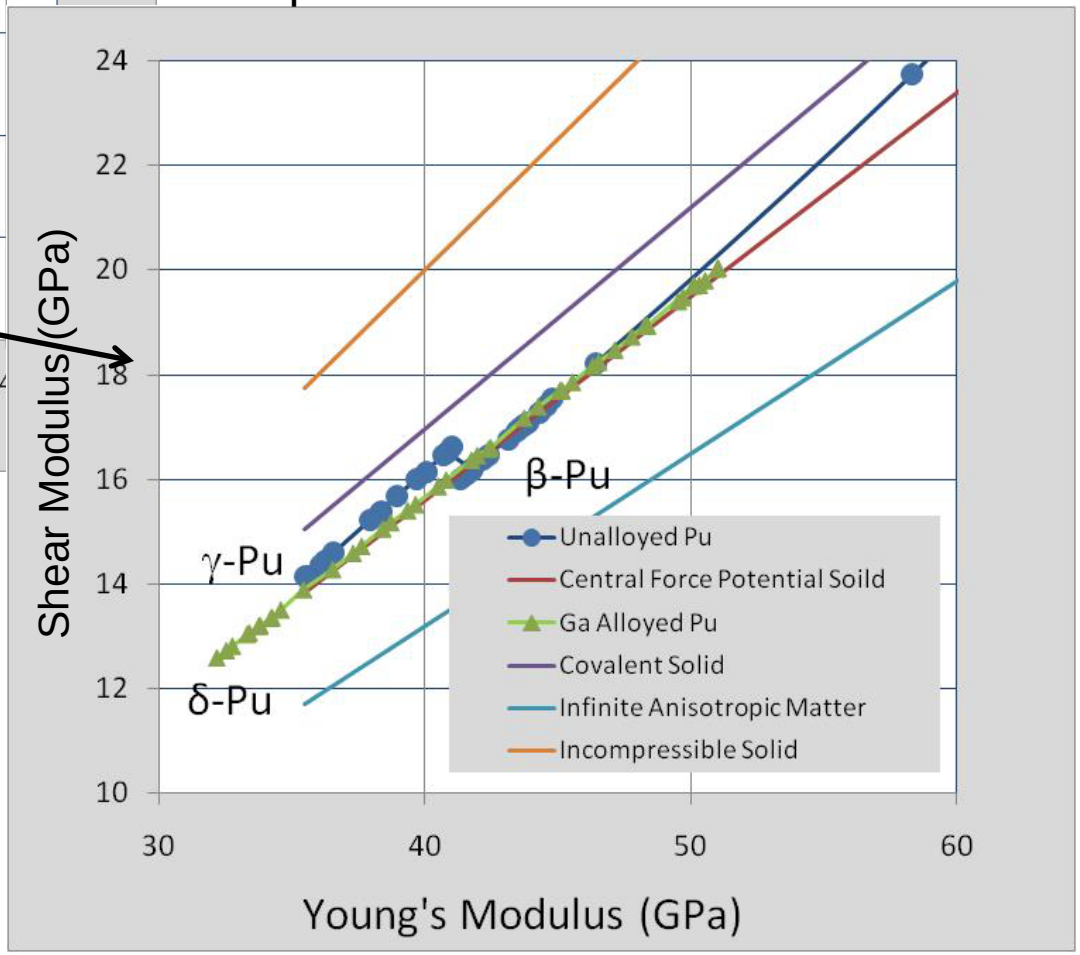
In Pu, interatomic bonding as observed in elastic properties exhibits a curious adherence to central force interatomic potential behavior independent of crystalline phase and alloying in single and mixed phase microstructures. **Valid for homogeneous, quasi-isotropic materials having central forces between atoms.**

Poisson Ratio	G/E	Solid's Bonding Character
0	0.5	Incompressible Solid
0.18	0.42	α-Pu: Covalent, Elastic Solid
0.24-0.30	0.39-0.40	β-Pu and γ-Pu: Indeterminate Nature
0.28	0.39	δ-Pu: Central Force Pair Potential through Next Nearest Neighbor (FCC and BCC Lattices)
0.5	0.33	Infinite Elastic Anisotropy (ex., liquids, polymers, etc.)

Bonding Behavior of Unalloyed δ-Pu and 2at% Ga Stabilized δ-Pu



The α→β transformation is identifiable as a changeover from covalency to a central force potential behavior.



The β→γ transformation is identifiable as a changeover from central force potential behavior toward covalency.

The δ-phase acts as a central force potential solid throughout our measured values.

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Covalent Bonding in α-Pu?

Of the 112 bond lengths between 8 unique Pu atomic positions in α-Pu nearly 30% are short bonds (≤2.8Å).

Whereas, of the 91 bond lengths between 7 unique Pu atomic positions in β-Pu only 9% are short bonds (≤2.8Å).

All other phases have no bond lengths ≤2.8Å.

Density of α-Pu is 19.86g/cc.

Covalency exhibited in $AnCl_6^{2-}$ Complexes (D.Clark)

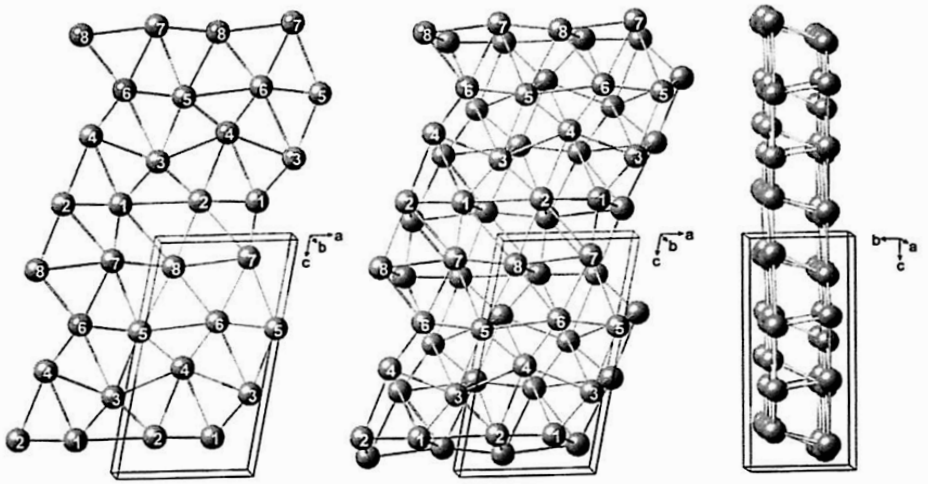


Fig. 7.22 *Several views of the monoclinic α-phase structure of plutonium with* 16 *atoms per unit cell and eight different atom positions.*

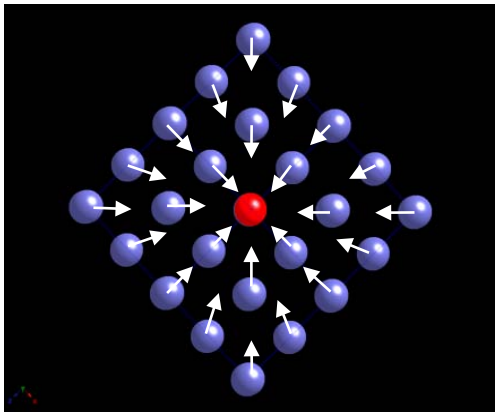
Table 7.10 *Structural parameters and bond lengths for α plutonium (Miner and Schonfeld, 1980).*

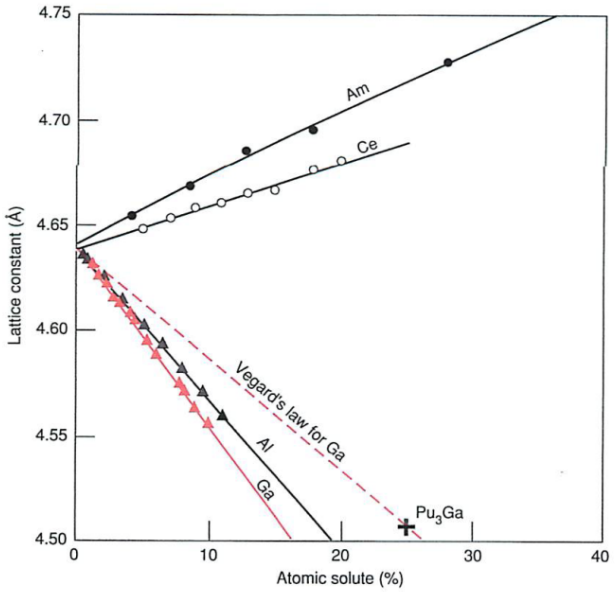
			Short bonds (Å)		*Long bonds (Å)*		*All bonds (Å)*	
Atom	*x*	*z*	*No.*	*Range*	*No.*	*Range*	*No.*	*Mean*
1	0.345(4)	0.162(2)	5	2.57–2.76	7	3.21–3.71	12	3.10
2	0.767(4)	0.168(2)	4	2.60–2.64	10	3.19–3.62	14	3.21
3	0.128(4)	0.340(3)	4	2.58–2.66	10	3.24–3.65	14	3.18
4	0.657(5)	0.457(3)	4	2.58–2.74	10	3.26–3.42	14	3.13
5	0.025(5)	0.618(3)	4	2.58–2.72	10	3.24–3.51	14	3.19
6	0.473(4)	0.653(2)	4	2.64–2.74	10	3.21–3.65	14	3.22
7	0.328(4)	0.926(2)	4	2.57–2.78	10	3.30–3.51	14	3.15
8	0.869(4)	0.894(2)	3	2.76–2.78	13	3.19–3.71	16	3.32

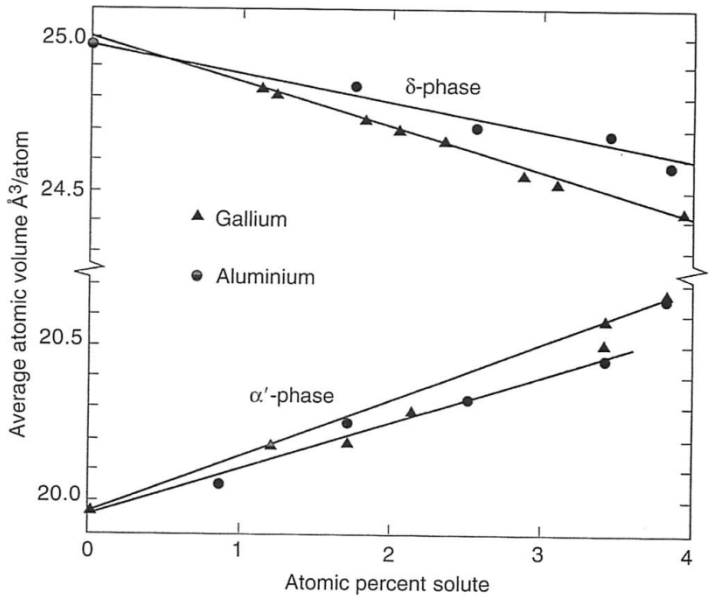
Ga Alloying: Disrupting Covalency in α-Pu

Ga act to disrupt covalent bonding in Pu:

- Ga atoms attract Pu atoms and contract the lattice in Ga stabilized δ-PuGa.
- Ga expands the lattice in monoclinic α-Pu







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Conclusions and Future Work

Conclusions

- Polycrystalline single δ-phase Pu (unalloyed and Ga alloyed) exhibit similar elastic properties, both in bulk and shear. In this temperature range, these materials demonstrates central force interatomic potential behavior.
- Otherwise, unalloyed polycrystalline Pu displays elastic properties which varies from covalent solid to central force interatomic potential behavior .
- Unalloyed α-phase Pu exhibits significant covalent bonding (short bonds) which is disrupted by Ga alloying or anharmonic effects induced at high temperatures;
- Ga at ~0.15 at% is soluble in α-Pu and these materials exhibit changes in phase transformation thermodynamic properties when compared with electro-refined unalloyed Pu;

Further Work

- Improve cast, fabricated and well-characterized unalloyed and Ga alloyed Pu.
- Measure temperature dependence of thermal expansion, specific heat, and elastic moduli for double electro-refined unalloyed Pu and Ga stabilized δ-Pu.