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# Temperature and time-dependence of the elastic moduli of Pu and Pu–Ga alloys

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**Abstract**

In previous work, on cooling from 300 K to 10 K the elastic moduli for both α- and δ-Pu dropped 30%. This large change may reflect effects of 5f-electron localization. In this work, the elastic moduli at ambient temperature of several Pu–Ga alloys were measured using resonant ultrasound spectroscopy (RUS). The strong temperature dependence of the bulk and shear modulus and the temperature independence of Poisson's ratio was confirmed and the upper temperature limit for α-Pu was extended to 360 K. Measurements of the time dependence of the shear moduli of Pu and Pu–2.36 at.% Ga were determined with high precision as a function of time and temperature. Using a model for time dependence of point defects, we determined the exponential time constant at ambient temperature for such variations. The low temperature results are consistent with Fluss [1].


*Keywords:* Plutonium; Elasticity; Ultrasound

## 1. Introduction

The elastic moduli (bulk, shear, Young's) are important properties for engineering, validation of ab initio, embedded-atom, and other models, and connect directly to fundamental thermodynamics. To measure elastic moduli, we used mechanical resonances and numerical fitting procedures to determine all the moduli at a given temperature with one measurement (RUS). RUS measurements are performed on samples that to good accuracy are free vibrators. Because a complete analytical solution for the free vibrations of even a rectangular parallelepiped resonator (RPR) does not exist, one must rely on approximations. Migliori et al. [2–4] give a complete treatment of this method.

## 2. Experimental

The elastic moduli are determined from measurements of the resonance frequencies using a RUS [4] system constructed entirely of ceramics, metals, and other inorganic materials to preclude deleterious radiolytic interactions during the very long times required to study aging. The system can operate between 1.8 K and 700 K. Several approaches to temperature control were taken in the results that follow, but the primary measurements were made in a He atmosphere. Temperature was controlled to about 1 mK, and, dependent on the sample shape errors, absolute accuracy is much better than 1%. The shape and dimensional errors of the RPR samples are the primary source of errors in the densities and elastic moduli. Therefore, considerable care was taken in producing accurately square and parallel samples. In the experimental results reported here, the dimensional errors were less than 5 μm.

## 3. Results and discussion

### 3.1. Survey of elastic moduli at ambient temperature

We surveyed elastic moduli at ambient temperature of Pu, Pu–Ga alloys and an alloy that, by introducing some $^{238}$Pu, "ages" at a rate 16.5 times that of normal $^{239}$Pu (the zero time is 15 May 2002). In Table 1 we summarize our results. We use standard crystallographic notation for our reported results such that $c_{11}$ determines the longitudinal sound speed $v_1 = (c_{11}/\rho)^{1/2}$, $c_{44}$ determines the shear speed similarly. For reference, note that the bulk modulus $B$ is $c_{11} - 4c_{44}/3$ while the shear modulus $G$ is $c_{44}$.

All measurements presented here were performed on fine-grained polycrystal, accurately polished rectangular parallelepiped resonator's (RPR) of known composition. With the dimensional errors given above, the errors in the total volume of the sample are less than 1.5%. With a mass determined to 0.1 mg, we compute density geometrically for each sample to within ± 0.2 g/cm$^3$. Slight rounding of edges and corners make

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Table 1
Elastic moduli and density for polycrystal Pu and Pu alloys at ambient temperature

| Sample | $c_{11}$ (GPa) | Bulk (GPa) | Shear (GPa) | Density (g/cm$^3$) |
|---|---|---|---|---|
| Single crystal δ-Pu 3.3 at.% Ga new [12] | 51.40 | 29.90 | 16.20 | |
| Polycrystal δ-Pu 2.36 at.% Ga new | 52.3 ± 0.15 | 30.60 | 16.3 ± 0.006 | 15.47 |
| Polycrystal δ-Pu 3.30 at.% Ga new 297 K | 51.8 ± 0.44 | 29.60 | 16.68 ± 0.018 | 15.70 |
| Polycrystal δ-Pu 3.30 at.% Ga 2 years 292 K Homog. | 52.7 ± 0.62 | 30.50 | 16.67 ± 0.025 | 15.70 |
| Polycrystal δ-Pu 3.30 at.% Ga 1.5 year 298 K | 51.8 ± 0.55 | 29.40 | 16.79 ± 0.025 | 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 ∼298 K | 53.90 | | 16.98 | 15.59 |
| Polycrystal δ-Pu 4.64 at.% Ga 11 months 295.87 K | 54.10 | | 16.96 | 15.59 |
| Polycrystal δ-Pu 4.64 at.% Ga 11 months 275.41 K | 55.05 | | 17.27 | 15.59 |
| Polycrystal δ-Pu 1.73 at.% Ga 15 years | 47.50 | 26.70 | 15.60 | 15.70 |
| Polycrystal δ-Pu 3.90 at.% Ga 15 years | 58.40 | 34.30 | 18.10 | 15.51 |
| Polycrystal δ-Pu 5.53 at.% Ga 44 years | 50.00 | 27.00 | 17.20 | 15.48 |
| Polycrystal δ-Pu$^{242}$ 5.5 at.% Al 1.5 year 298 K | 51.28 | 27.90 | 17.51 | 15.74 |
| Cast α-Pu [13] | 104.60 | 46.60 | 43.50 | |
| Cast α-Pu (new) 297 K | 112.80 | 54.40 | 43.70 | 19.70 |
| Polycrystal δ-Pu 238/239 1.8 at.% Ga 3 months 295 K | 51.30 | 29.70 | 16.20 | 15.69 |

The densities we estimated from dimensions and mass are consistently slightly low. The values here may be corrected to the best known density for each alloy if desired. The approximation time between arc melting and measurement is indicated.

the geometrically determined density reported here on the low side of the error bars. This is not the most desirable approach to determining density, but it does provide a measure of sample quality, and, in the case of the $^{242}$Pu–5 at.% Al sample, the relatively high density confirms the presence of martensite, also observed metallographically. It is expected that some formation of mechanically induced α-Pu has occurred in δ-Pu specimens. However, because all samples are at least as large as a 2 mm$^3$, minimal errors in absolute moduli are expected from this effect.

### 3.2. Elastic moduli versus temperature

The reported temperature dependence of the elastic moduli for Pu alloys is unusual, exhibiting more than a 30% drop from 10 K to 300 K [5,6]. This is particularly important to both engineering and to fundamental properties because the changes are an order of magnitude greater than in other metals. For example, Pu–2.36 at.% Ga exhibits a 10% change in $B$ and $G$ over a temperature range comparable to that seen outdoors from normal seasonal variations. This change is more than an order of magnitude larger than that for Al, Cu and steel. In addition, the fractional temperature dependences of both $B$ and $G$ are nearly identical, suggesting one physics driver is responsible. A potential driver is the localization of the 5f-electrons. We stress that in most metals $G$ varies more strongly with temperature than $B$.

In Fig. 1 we show the fractional change in both $B$ and $G$ for a $^{242}$Pu 5 at.% Al δ-Pu specimen. A metallographic polish revealed martensite needles (so-called α-prime). This is consistent with the slightly high density of the material, presented in Table 1. Similar results for δ-$^{239}$Pu 2.36 at.% Ga are reported elsewhere [6].

The elastic moduli of polycrystal zone-refined and arc-cast Pu (α-Pu) from 10 K to 360 K are shown in Fig. 2. Elastic moduli determined by RUS are linearly proportional to density, and may be corrected for true density if desired. For this measurement, the sample was polished into a rectangular parallelepiped resonator (RPR) with dimensions of 0.222 cm × 0.2323 cm × 0.2032 cm. The density from weighing and measuring the dimensions was 19.70 g/cm$^3$ consistent with this somewhat imprecise way of determining density. From analysis of the spectrum of mechanical resonances, we determined that certain frequencies were dependent only on $G$. We observe a nearly identical temperature dependence of both $B$ and $G$, with concomitant observation of a Poisson's ratio independent of temperature.

It is surprising that both α- and δ-Pu 2.36 at.% Ga exhibit nearly the same fractional softening on warming from 10 K to 300 K [5,6], and as we report here, that trend continues for α

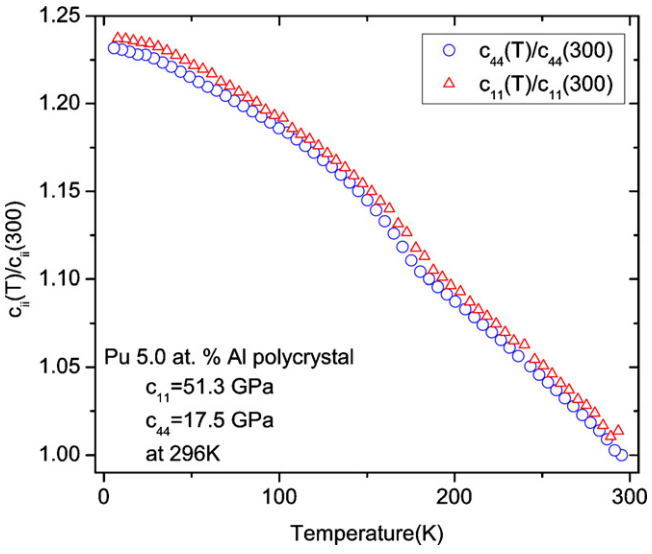


Fig. 1. $^{242}$Pu–5 at.% Al δ-Pu specimen with microstructural analysis indicating some martensite (α-prime). The martensite transition is clearly visible at 180 K. Based on the ratio of the elastic moduli of α- and δ-Pu and on the deviation from a smooth curve, we estimate that about 5% of this sample is α-prime. We observe a nearly identical temperature dependence for both the shear and compressional moduli. Absolute moduli can be obtained by using the 300 K values of Table 1 and the fractional changes from this figure.

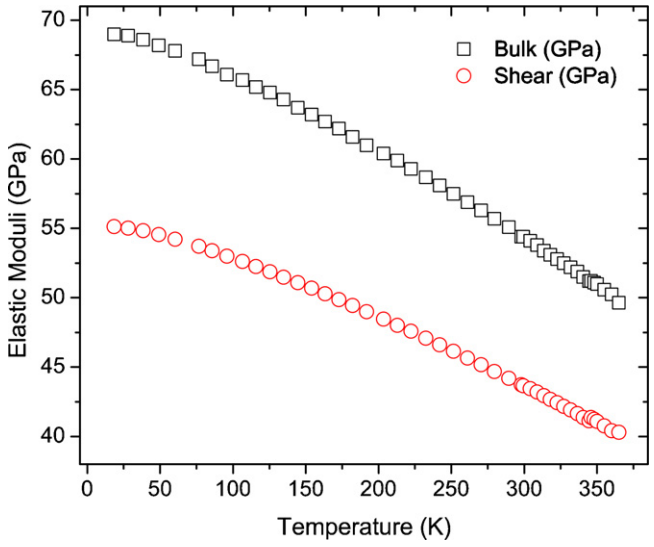


Fig. 2. The elastic moduli of α-Pu from 10 K to 360 K. A constant Poisson's ratio indicates that the temperature dependence of the bulk modulus and the shear modulus are the same. The measurements below 300 K are from [5].

above 300 K. Note that these measurements were performed in the extreme elastic limit, so stiffening and softening refer precisely to elastic moduli, not hardness. We note from previous work that δ-Pu 2.36 at.% Ga exhibits a negative volume thermal expansion coefficient above 350 K [7], that is, the sample volume decreases on warming above this temperature, but, opposite to what most solids do as their volume decreases, the elastic moduli decrease as well. A nearly inescapable prediction is that the bulk modulus of δ-Pu must decrease under pressure, at least below some indeterminate-as-yet pressure [8,9].

### 3.3. Elastic moduli versus time

To understand the variation of the elastic moduli with time in Pu one must keep in mind several effects:

1. Pu–Ga alloys are not thermodynamically stable at ambient temperature, as the "Russian" phase diagram shows [10]. Although the reversion to Pu and $Pu_3Ga$ may take a very long time, the half-life of $^{239}Pu$ is very long as well, and therefore, such effects cannot be discounted immediately;
2. As $^{239}Pu$ decays radioactively, interstitial-vacancy ("Frenkel") pairs are produced, about 2200 decay$^{-1}$. The Frenkel pairs are also not thermodynamically stable and display strongly temperature-dependent lifetimes, spanning from picoseconds to years;
3. Decay products include He and metals that are not Pu, and so can change physical properties.

A few key referents include:

1. From radioactive decay, $3.16 \times 10^{-9}$ of the Pu atoms present in a specimen decay per hour,
2. $6.9 \times 10^{-6}$ Frenkel pairs/(h atom) are produced,
3. From Table 1, using the measured moduli of Pu 3.3 at.% Ga measured soon after arc melting and 15-year-old Pu 3.9 at.% Ga, and noting from the table the very weak dependence of moduli on Ga concentration on this concentration range, we infer that the differences are primarily caused by aging. This places a bound on the maximum long-term fractional rate of change of the bulk modulus of order $9 \times 10^{-7}\,h^{-1}$,
4. It is well known that the elastic moduli respond strongly to changes in mass density or retained Frenkel pair density, typically an order of magnitude stronger. Thus from the raw Frenkel pair production rate, we can estimate that the elastic moduli change at a fractional rate always less roughly $7 \times 10^{-5}\,h^{-1}$. Because most Frenkel pairs recombine in microseconds at ambient temperature, these rates are absolutely limiting, and apply to radioactive decay at very low temperature (10 K). At ambient temperatures, the rates must be lower. Any rate substantially different from these must be associated with other physical effects.

It is important to note that the aging effects seen are much smaller than the error bars for measurements presented above. This is because the precision of RUS for Pu specimens is of order 5 parts in $10^7$, but absolute accuracy is limited by errors in the dimensions, of order several tenths of a percent. We can, therefore, observe part-per-million changes in moduli versus time without knowing the values of the moduli to this precision. Thus the effects observed by making high-precision measurements of the elastic moduli versus time are not detectable by making measurements on two different samples with age differences less than a few years. It is also clear that measurements of different specimens with age differences of even 15 years is at the limit of our ability to resolve changes in time.

Time-dependent measurements were made using a very-high-precision temperature control system that held temperatures to within a mK over many days and a somewhat less precise system with no temperature control. This second system was used to measure an alloy with approximately 1.8 at.% Ga at 295 K that had the same Ga concentration as the alloy containing some $^{238}Pu$. Good temperature measurement is crucial because of the strong temperature dependence of the elastic moduli of all samples.

We can immediately eliminate the issue of phase stability at time scales shorter than many hundred years, consistent with the analysis of Turchi [11] because the retention of radiation damage at low temperatures, and the subsequent annealing out at higher temperatures is very similar in α- and δ-Pu shown in Figs. 3 and 4. If phase stability were dominant, α-Pu would show substantially different behavior from δ-Pu. Thus, because the damage annealing rate must be similar for α and δ, and α shows very weak long-term changes at constant temperature, Fig. 5, we can conclude that the short-term effects we observe in both α and δ are not associated with phase stability.

We introduce a model for the stability and time dependence of point defects based on linear relaxation, and we illustrate it with an electrical circuit analog. The circuit has three elements: (1) a current source which is the number of Pu disintegrations per second, (2) a "capacitor" C which is Pu metal as a storage system

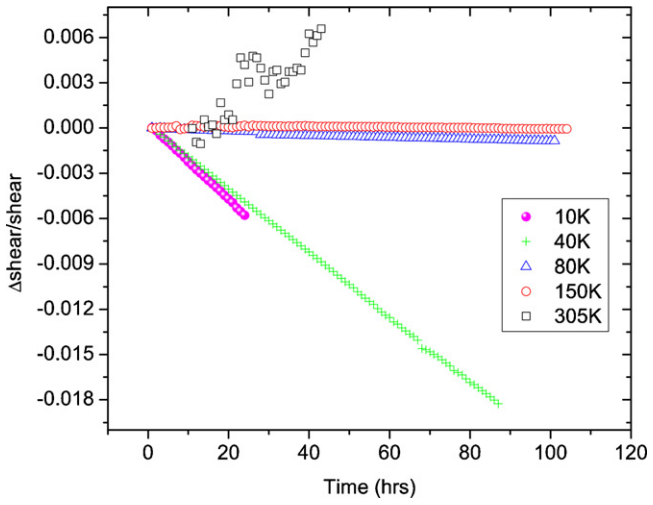


Fig. 3. The normalized shear modulus change for α-Pu vs. time and temperature. We began taking data after the initial rapid transient decayed.

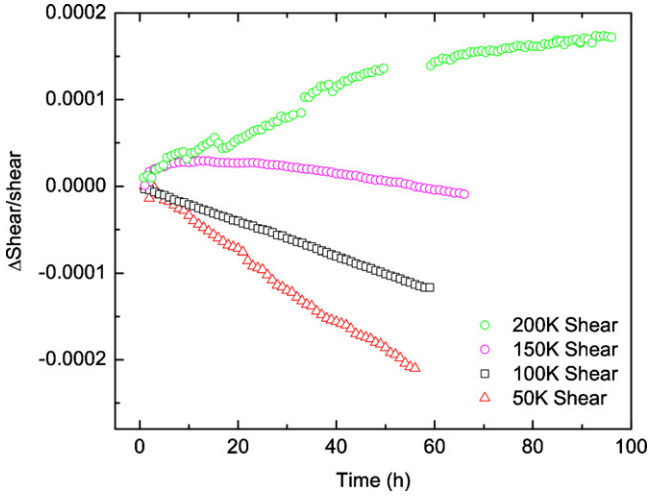


Fig. 4. The normalized shear modulus change for Pu 2.36 at.% Ga vs. time and temperature. Note that for this measurement we began taking data before the initial rapid transient decayed.

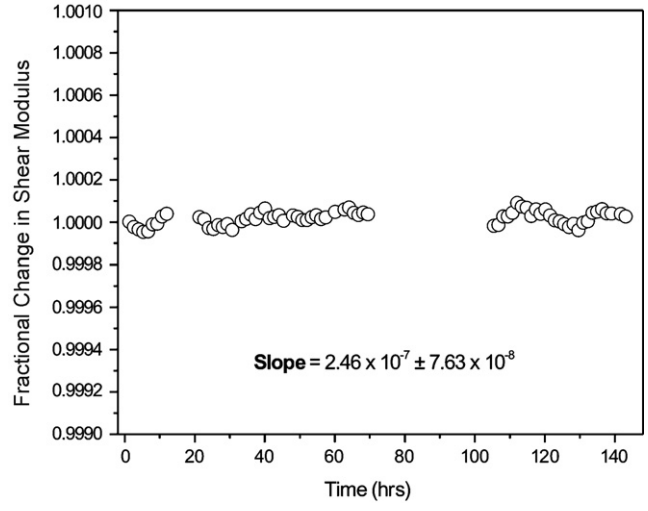


Fig. 5. The fractional change in shear modulus for α-Pu. Measurements made on a sample stored at ambient temperature and measured at ambient temperature showing negligible change of properties with time.

for point defects, and (3) a resistor R to model thermally driven point-defect recombination, in parallel with C that "leaks" away point defects, and which depends on temperature. If our model produces time constants shorter than $\tau = 34{,}780$ years (this is the exponential time constant for a half-life of 24,100 years) then the approximations are potentially valid.

$$P = P_0 + P_{\text{aging}}\, e^{-t/\tau}$$

In this model, $P_0$ is the property value (in this case shear modulus) reached after long times; $P_{\text{aging}}$ the maximum property change with age; $\tau$ is the exponential time constant.

This is a linear model with certain implications. Obviously, as radiation damage accumulates the shear modulus changes with time. The total damage retained is dependent on the decay rate, but it is not so obvious that the time to reach a given fractional damage level does not depend on decay rate. The time constant for point-defect retention must be independent of whether we use $^{239}$Pu (239 alloy) or $^{238}Pu_{0.06}$ $^{239}Pu_{0.94}$ 1.8 at.% Ga (238 alloy), but the final damage levels are. We do, in fact, have enough information to compute $P_{\text{aging}}$. Because the decay rate for the 238 alloy is 16.5 times that of a 239 alloy, we can assume, to an accuracy of about 1 part in 16, that the difference between the shear moduli of these alloys is approximately $P_{\text{aging}}$. Unfortunately, we cannot make an exact comparison because the exact Ga concentrations were not available in a 238 alloy, so we use the 2.36 at% Ga alloy for the 239 alloy. We find the difference to be 2%. Even though this difference could be in error by a factor of 3 because of uncontrolled variables, the real conclusions will still stand. Also, if our measurements (3 real months old for the 238 alloy, about 6 months for the 239 alloy) were at asymptotically long times, and if the computed time constant is less than 3 months, the assumptions behind this model are valid.

$P_{\text{aging}}$, for the 239 alloy at ambient temperature is, from the model, 2%/16.5 = 0.12% because the source term for radiation damage is this much lower than for the 238 alloy. This now provides sufficient information to compute $\tau$. Using the measurements of the time dependence at ambient temperature of the 239 alloy to determine $\tau$ $P_0/P_{\text{aging}}$ near 300 K, we obtain $\tau = 8$ days. Therefore, in about 40 days (five time constants), the properties changed by point defects of any radioactive Pu sample stabilize to 99% of their final value. This time is short enough to validate all the above assumptions, and is consistent with the work by Fluss [1] on susceptibility at low temperatures, because ours and his time behavior are similar.

We conclude, therefore that Pu–Ga alloys exhibit negligible aging associated with phase stability issues, that the point-defect density reaches a steady state in times of order 1 month, that this steady state is a competition between the radioactive production rate and the temperature-dependent annealing rate. Thus radiolytic products such as U and He must be the primary agents for aging of Pu–Ga alloys.

## 4. Conclusions

Using RUS to measure polycrystal Pu and Pu–Ga alloys the elastic moduli of some Pu–Ga alloys are surveyed, the upper temperature limit for elastic moduli of monoclinic (α) Pu is

extended and the relative changes with time of the shear moduli of selected Pu and Pu–Ga alloys were determined with very high precision to improve the understanding of aging. Aging effects from phase stability drivers appear negligible, aging associated with radiation-induced point defects stabilizes in a month or so with maximum changes much less than a percent. Thus the primary aging mechanism for the physical properties of Pu–Ga alloys appears to be changes induced by He, U, and other radiolytic products.

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