

A Single-Crystal Saga

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From 1963 to about 1976, Roger Moment of Rocky Flats attempted to grow single crystals of gallium-stabilized, δ -phase plutonium that were suitable for measurements. He finally succeeded and was able to make what are still the only measurements of the elastic constants of a single crystal of δ -phase plutonium. The staff of Los Alamos Science are pleased to present his story.

The early 1960s were truly a “golden era” in metallurgy within the weapons complex. While many research programs were being conducted at Los Alamos Scientific Laboratory and Lawrence Livermore Scientific Laboratory, limited research efforts were also taking place at other “production” sites such as Rocky Flats. Weapons budgets during those years were generous, and Rocky Flats staffed its metallurgy and chemistry groups with many new members holding doctorate degrees. Although their primary responsibility was to support the main objective of pit production, the staff members were also encouraged to spend a portion of their time pursuing any scientific research they thought would be of value. I had spent my graduate years growing and measuring properties of single crystals, and when I showed up at Rocky Flats in September

1963, it was only natural that I would try and see whether similar work might be done with plutonium.

During that same period, Roland Fisher, who was also at Rocky Flats, was attempting to grow a single crystal of α -phase plutonium by allowing the liquid metal to solidify while being kept under high pressure. Not wanting to duplicate effort, I turned my attention to growing single crystals of the gallium-stabilized δ -phase.

Conducting plutonium research experiments was quite easy in those days, compared with now. We set up our furnaces in a small glove box and did the encapsulation in an open-faced hood. My experimental operator¹, Jim Parker, was skilled at working with small items, using the standard 0.76-millimeter-thick, lead-lined gloves, and he handled all the delicate operations without incident. We were most con-

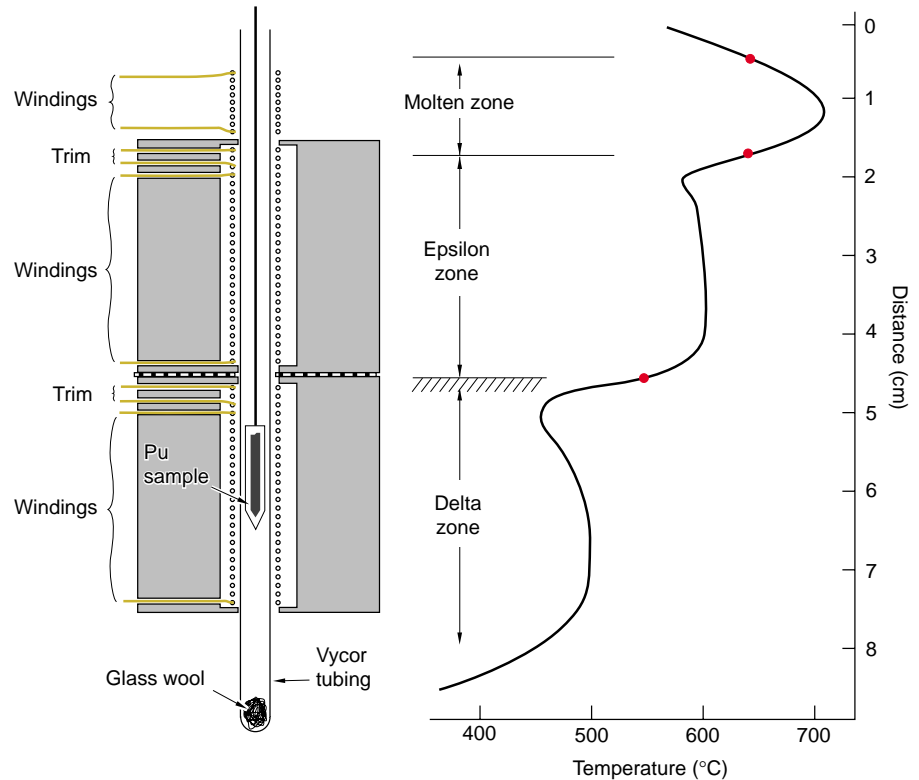
cerned about potential breakage of the sealed, evacuated glass tubes that held the plutonium and designed our equipment with containment layers—just in case. When the furnaces were finally dismantled after approximately 10 years of use, they were still uncontaminated.

My experience had been in growing crystals from the melt, and I thought that approach would be worth an initial try. If a large ϵ -phase crystal could be formed upon solidification, then slow, directional transformation into δ -phase might still result in retention of large grains. Although I had expected some difficulties with this approach, I did not fully appreciate all the problems created by the solid-state

¹Much of the workforce at Rocky Flats was unionized. The Experimental Operator classification was used for support personnel who worked in R&D and performed most of the hands-on operations with plutonium and our test equipment.

Figure 1. Schematic of Multistage Furnace

We used multistage furnaces to melt and then recrystallize gallium-stabilized, δ -phase plutonium. The furnaces were constructed from stainless steel cylindrical blocks. Nichrome wire, used for heating, was wrapped around a Vycor™ tube running through the middle of the blocks. Trim windings created a smooth yet steep temperature gradient through the phase-transition zones, as seen in the temperature profile on the right. The plutonium sample was enclosed in a pointed Vycor™ capsule and slowly lowered through the tube. The plutonium would melt, solidify in the ϵ -phase, and then transform to the δ -phase. The glass wool pad was inserted to prevent the inner capsule from breaking should its suspending wire break.



transformation from ϵ - to δ -phase.

A fairly simple, multistage furnace was constructed, which consisted of a series of ovens, each oven cooler than the one preceding it. Gallium-stabilized δ -phase plutonium (1 wt % gallium) was placed in a Vycor™ capsule that was drawn to a fine point at one end. The capsule was then lowered point first through the furnace by a primitive clock motor system, as seen in Figure 1. The drop rate was usually 0.76 to 3.3 millimeters per hour.

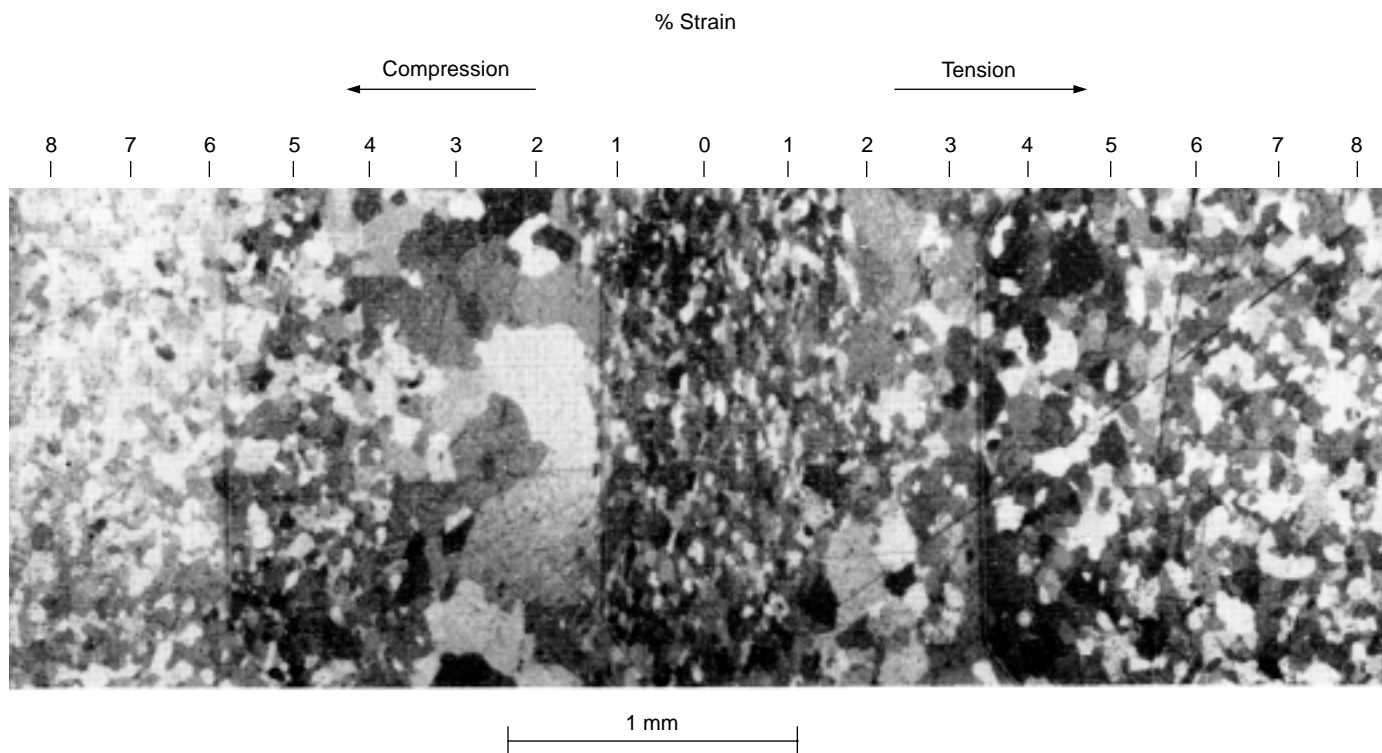
The metal liquefied in the top furnace and transformed into ϵ -phase as it entered the middle furnace. Solidification first occurred in the capsule's point, but only a few grains could grow within that small volume. We hoped that one of those grains would grow larger at the expense of others as the rest of the melt solidified and transformed into ϵ -phase. As the capsule entered the lower oven, we hoped that the ϵ -phase grain would smoothly transform into one or a few large δ -phase grains.

We tried this solidification tech-

nique for years and grew many large grains ranging from 3–4 millimeters in their largest dimension, but in the end, we could not use those grains to make any measurements. Back-reflection-Laue x-ray diffraction, which gives detailed information about the crystallographic quality of grains, showed that most of the large grains were polygonized; that is, they were composed of several subgrains that were slightly misaligned to each other. As such, the grains were not suitable for high-quality physical-property measurements. Furthermore, a 4-millimeter-long grain imbedded in a plutonium rod was simply not usable. The measurements required the grain to be isolated, but typically one-third to one-half of the sample volume was polished away during metallography (that is, the polishing and subsequent etching of a metal surface that helps to visualize the grain structure). By the time we extracted the grain, too little of it was left, and using it in physical-property measurements became almost impossible.

We were never able to determine why the solidification technique was unsuccessful. One reason might have been the internal conditions resulting from coring, or alloy segregation within a grain. When an alloy freezes from the melt, the composition of the solid that forms varies, depending on how the alloying element partitions itself between the liquid and solid states. In the case of the plutonium-gallium alloy, the first bit of ϵ -phase grains to solidify from a nominally 1.0 wt % plutonium-gallium alloy have a composition of about 1.5 percent by weight gallium. As the temperature drops, new material accretes onto the grain, but the percentage of gallium in the next material to solidify is less.

Coring due to the liquid to ϵ -phase transformation was probably negligible, since the diffusion rate for gallium in the ϵ -phase is very high and there would have been ample time during that transition for homogenization to occur throughout each grain. But similar coring takes place during the ϵ - to δ -phase transformation, and the



diffusion rate for gallium in the δ -phase is substantially slower. Even though I did not know what effect all this would have on grain growth, I anticipated there might be some problems. Additionally, the crystallographic substructure in those large grains that had been grown may well have been a consequence of both coring and the solid-state transformation. I therefore wanted to try crystal-growing techniques that would avoid these complications.

A method that takes place entirely within the room-temperature phase is strain anneal. A minimum amount of strain is introduced into a specimen, just enough to cause new crystals to form and then grow when the specimen is heated to an elevated temperature. This process relieves internal stresses through a number of mechanisms and lowers the total-energy state through grain-boundary migration.

If the number of growing grains can be kept to a minimum, they will consume the surrounding matrix and produce a material composed of only a

few large grains. At the “critical” strain, relatively few grains become “active,” and those that do are able to grow into the surrounding matrix with minimal competition from others. During this grain growth, a structure of high crystallographic perfection is formed, and some grains can become large, their dimensions being often limited only by the size of the specimen. To succeed in obtaining these large grains, however, one needs to anneal at fairly high temperatures. In the case of plutonium 1.0 wt % gallium, we could heat specimens to 500°C and still be well within the alloy’s room-temperature stable δ -phase.

I first needed to determine the critical strain that would be required to initiate limited recrystallization and grain growth. I did this by bending a small plutonium strip around a curved mandrel, thereby introducing strains that ranged from compressive at the inner diameter, through zero, to tensile at the outer diameter (see Figure 2). A high-temperature anneal caused recrystallization to occur in high-strain regions

Figure 2. Critical Strain
Bending a plutonium (1 wt % Ga) alloy strip around a mandrel created a range of strains, both tensile and compressive, about a central neutral axis. Annealing the strip at 500°C for three days allowed those grains in the region of critical strain to grow the most. As seen in this photomicrograph, the critical strain appears to be around 2–3 percent.

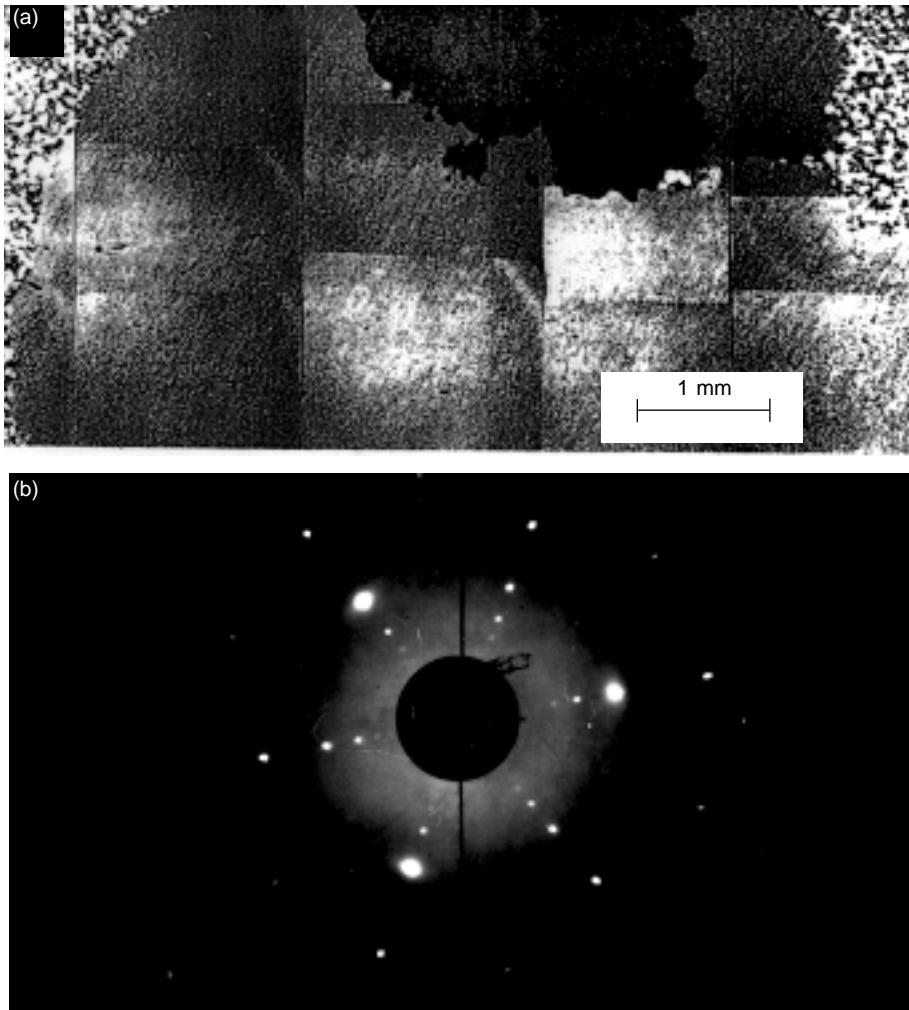


Figure 3. Single Crystals of Plutonium

(a) The grain shown here, grown by a strain-anneal technique, was more than 7 mm across. It lengthened to nearly 9 mm after a second anneal. Unfortunately, much of it was polished away in the course of performing metallography. The remaining grain had no more than 2 mm in depth and was not suitable for elasticity measurements. (b) Many of the crystals grown by strain anneal displayed a high degree of perfection, as indicated by sharp points in the back reflection Laue x-ray films. The crystal used for this Laue photograph was oriented normal to a $[111]$ axis.

and extensive grain growth in others. The largest grains that resulted were located in the specimen in which approximately 2 to 3 percent of the strain had occurred.

We therefore took a bar of δ -phase plutonium that was about 5 millimeters squared in cross section—total impurity level less than 150 parts per million (ppm) excluding oxygen²—and strained it about 2 percent in tension. A point was shaped on one end that was then

electropolished to remove any surface contamination. We placed the specimen in a Vycor™ capsule and lowered it slowly into a furnace, where it was annealed for three days at 500°C. One very large grain (7.5×3.5 millimeters) was found although it was not located at the sample tip, as had been expected. (See Figure 3.) This grain grew further to a maximum length of 9 millimeters after an additional 7-day anneal. However, its maximum thickness was only 2

millimeters, and it would have been impossible for us to isolate it and still preserve a crystal suitably large for the elasticity experiments we had planned. Back reflection Laue x-ray diffraction showed it to be quite perfect, as one would expect.

This crystal-growth approach was repeated many times, but we could not achieve consistent or repeatable results. Partly out of frustration, we also tried cycling through the solid-state ϵ - to δ -phase transformation. Instead of applying an external stress, we would have plutonium metal transform between those two phases several times. I reasoned that there might be some transformation-induced stress that could initiate grain growth in the δ -phase.

A rod 4.3 millimeters in diameter was pointed at one end and slowly lowered through two ovens with steep temperature gradients, first to transform it into ϵ -phase and then to transform it back into δ -phase. This double transformation cycle was repeated three times, followed by a 5-day anneal at 500°C to encourage grain growth. Metallographically polishing one side of the rod revealed a fine grain structure but also two large grains filling the diameter. One of the grains was 7 millimeters long. A 3-millimeter-thick section of this larger grain was cut from the rod, and its opposite faces were polished flat and parallel. Back reflection Laue x-ray diffraction showed a high degree of crystallographic perfection and the polished surface to be oriented 4° from a $[110]$ direction in a $\{001\}$ plane. These features made the sample extremely suitable for measurements of its elastic properties. The result of that work (see Figure 4) was published in 1976 (Moment and Ledbetter).

Because plutonium is radioactive, any crystal quickly becomes radiation-

²The presence of significant levels of impurities can limit grain growth because precipitates will arrest and pin the movement of grain boundaries as they sweep through the matrix. Our starting material was the purest available at the time; it typically contained about 120 ppm of impurities, excluding oxygen.

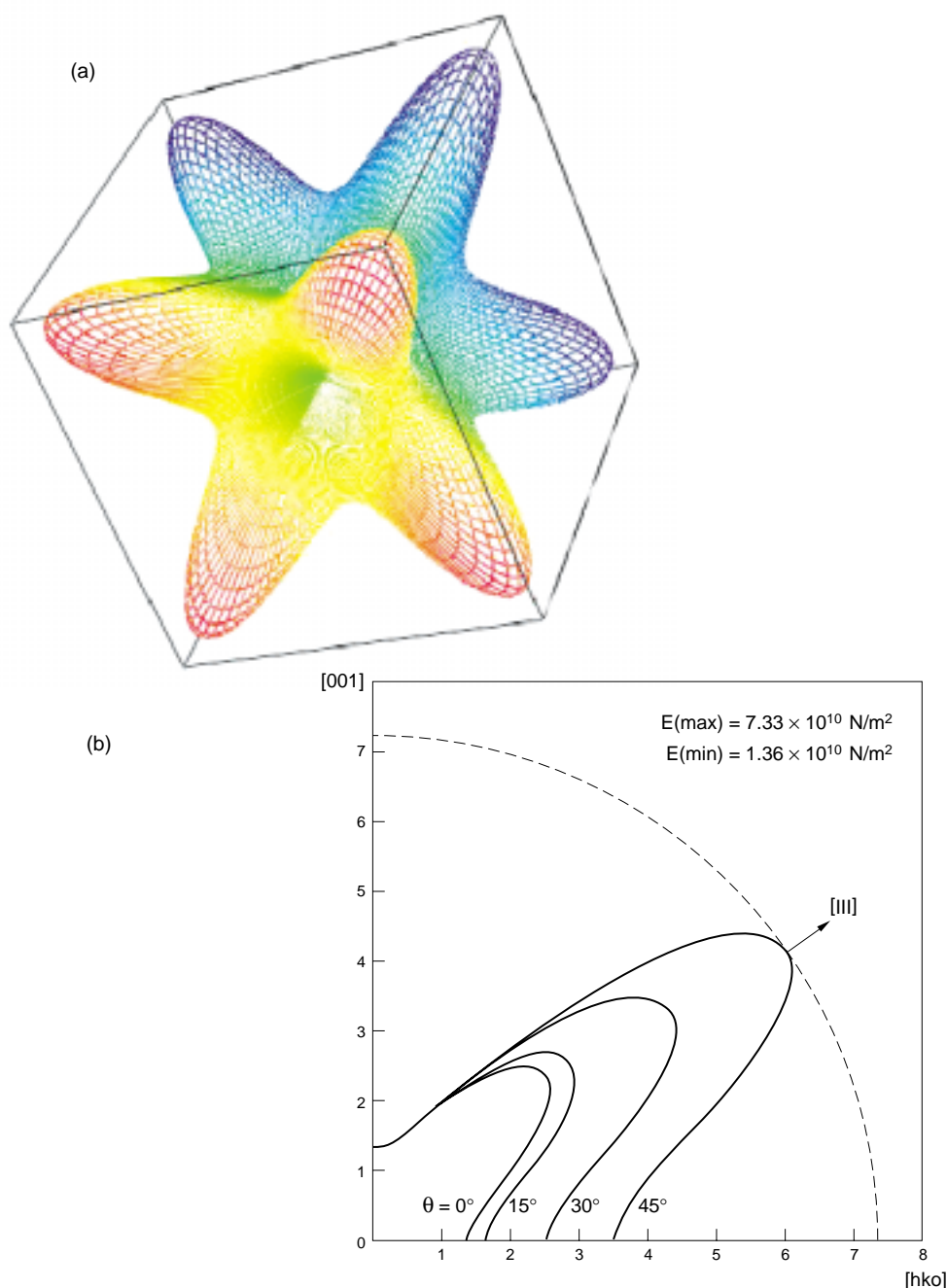


Figure 4. Young's Modulus in δ -Phase Plutonium

Single-crystal elastic constants were measured on the one large grain that was finally grown and isolated. (a) This graphic depicts the variation of Young's modulus (the ratio of applied tension to deformation in a direction parallel to the tension) in δ -phase plutonium as a function of direction in the face-centered-cubic crystal. The response of a single crystal to stress is highly anisotropic. As seen in the graph in (b), the ratio of maximum to minimum values is approximately 5.5, that is, δ -phase plutonium is more than five times stiffer in the [111] than in the [001] direction.

damaged and ceases to be useful for measurements of fundamental parameters. There is a constant need for new samples. But none of our efforts ever resulted in a technique that could be used to reliably provide crystals large enough for measurements of physical properties. The one successful experiment showed that some proper combination of parameters would work, but we did not know what all of these might be. Metal purity was probably an issue, as the best material we had to work with contained about 120 ppm, not including oxygen.

As I look back on this work, I can see many questionable decisions that we made and numerous areas for improvement. Today, we certainly have a much better understanding of the various metallurgical processes taking place. In addition, new technologies present opportunities to exercise greater control over the experimental technique. For example, levitation furnaces are now available for chill-casting high-purity samples with a very fine grain size. Zone-refining techniques are also available for consistently producing metal with an impurity content around or below 100 ppm. All these achievements provide an opportunity to revisit the growing of plutonium alloy grains under conditions that are greatly improved by comparison with those available 20 to 30 years ago. Hopefully, we will find a way to produce single crystals of plutonium in a repeatable fashion. ■

Further Reading

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- Moment, R. L. 1968. *J. Cryst. Growth* **2**: 15.
- Moment, R. L. 1966. *J. Nucl. Mater.* **20**: 341.