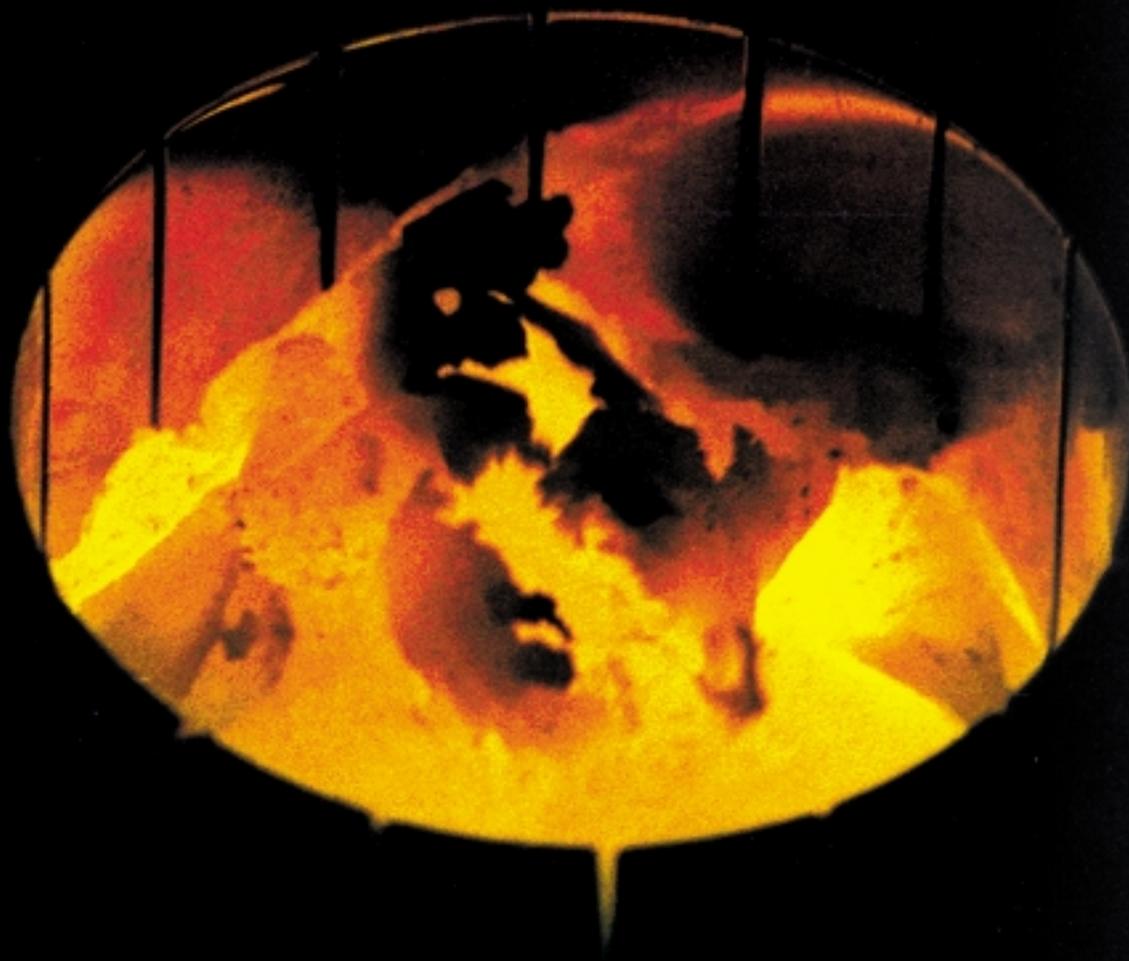


# Preparing Single Crystals of Gallium-Stabilized Plutonium

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Americium and gaseous impurities bubble from the surface of molten plutonium. The sample remains levitated within the vertical crucible of a vacuum distillation furnace. Such preparations are used to create ultrapure samples from which are grown single crystals of gallium-stabilized  $\delta$ -phase plutonium.

Scientists need large single crystals of plutonium to determine many of the fundamental properties of this metal, such as its electronic structure and atomic vibrational modes. In general, the electronic structure of a crystalline solid governs bonding, magnetism, and elasticity. The vibrational properties become increasingly important as the temperature of the material increases.

Because the electronic structure and vibrational modes of metals reflect the underlying symmetries of the lattice, which is never spherically symmetric, those properties always have a directional dependence. But measurements on polycrystalline samples cannot reveal that directionality because probing a polycrystal is akin to averaging over all crystal directions. Only a single crystal, as an extended, regular array of unit cells, can yield directional information. But single crystals of plutonium do not currently exist.

A program was recently initiated at Los Alamos to prepare plutonium and then grow large single crystals of gallium-stabilized  $\delta$ -phase plutonium. Our samples must be prepared from metal of the highest purity, because the electronic structure and vibrational modes of plutonium are highly affected by the presence of trace elemental impurities and alloy compositions. The required crystal size depends on the measurement techniques. For example, photoemission spectroscopy measurements of the density of electronic states require crystals on the order of 1 cubic millimeter. Resonant ultrasound spectroscopy measurements of the elastic constants need crystals a few cubic millimeters in size. Finally, inelastic-neutron-scattering experiments, which probe the phonon spectra, require single crystals of plutonium-242 that are

as large as 1 cubic centimeter. (Plutonium-242 has a smaller neutron-absorption cross section than plutonium-239 and is the favored isotope for the scattering measurements.)

In this article, we review solidification and solid-state methods for growing plutonium crystals and explain why it is difficult to grow single crystals of the required size. We then

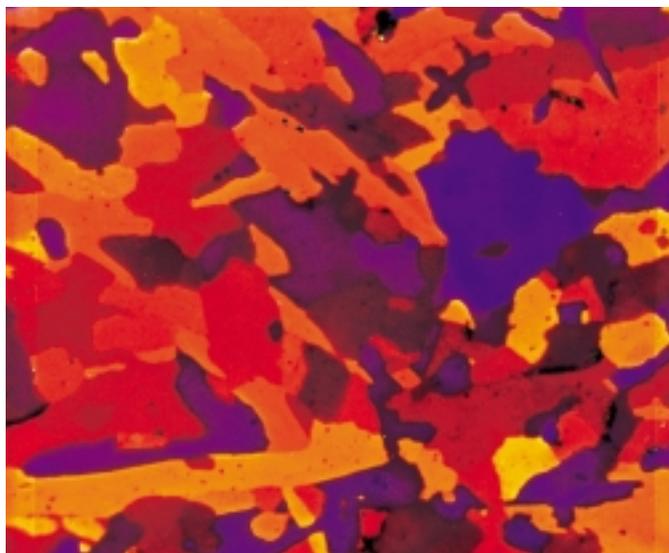
to each other in an orderly fashion because an equilibrium position is reached between attractive and repulsive forces.

It is very difficult, however, to grow single crystals of pure plutonium by simply letting the melt solidify. The pure metal passes through six allotropic phases ( $\epsilon$ ,  $\delta'$ ,  $\delta$ ,  $\gamma$ ,  $\beta$ , and  $\alpha$ ) as it solidifies from the melt and cools to room temperature. In each new phase, the plutonium atoms shift positions to form a new crystalline structure with a different density. Any large crystal grains that develop early in the cooling process become disrupted with each subsequent phase transformation. The result is invariably a polycrystalline solid. (See Figure 1.)

In the 1960s, scientists at Argonne National Laboratory grew single crystals of  $\alpha$ -phase plutonium by allowing the molten material to cool under 55 kilobar of pressure. Under those conditions, plutonium solidifies directly into the  $\beta$ -phase and transforms to the room-temperature stable  $\alpha$ -phase at 420°C, rather than at 112°C, as it does at ambient pressure. (The higher temperature means that the atoms are relatively mobile as they begin to form  $\alpha$ -phase grains.)

Furthermore, the metal does not change volume in going from the  $\beta$ - to the  $\alpha$ -phase at 55 kilobar. The combination of those advantageous properties allowed researchers to grow large grains, which were then cut from the surrounding matrix and polished into single crystals. Al Arko, who is now at Los Alamos, measured the resistivity and magnetic susceptibility of some of those  $\alpha$ -phase single crystals.

Also during the 1960s, Roger Moment of Rocky Flats tried to grow large grains of gallium-stabilized  $\delta$ -phase plutonium. At gallium concentrations between 1 and 2 weight percent (wt %), the plutonium-gallium alloy exhibits

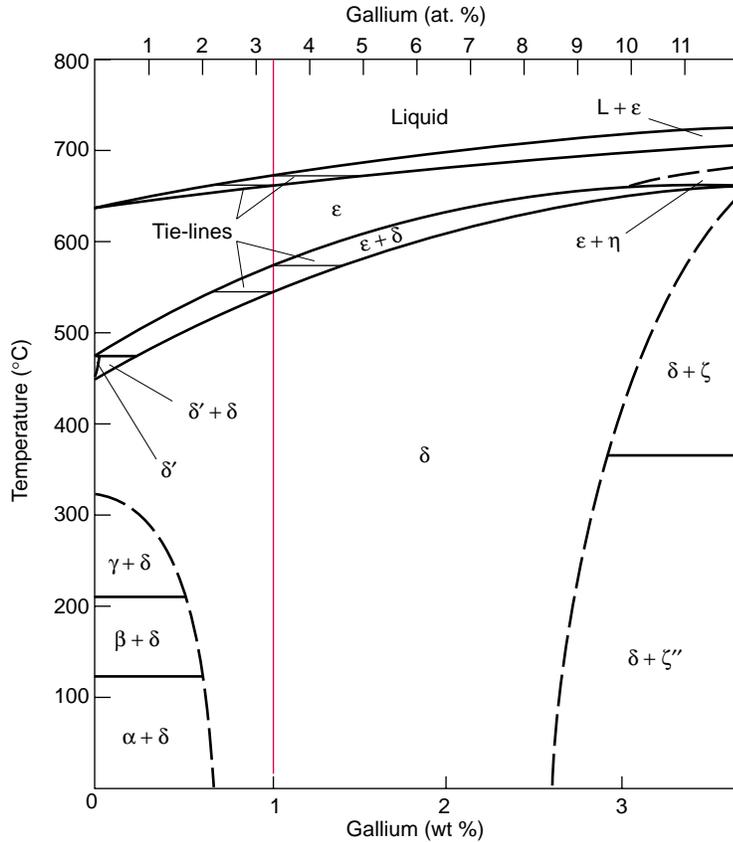


**Figure 1. Polycrystalline Plutonium**  
Gallium-stabilized,  $\delta$ -phase plutonium invariably solidifies into a multigrain structure. This sample of  $\delta$ -plutonium (1 wt % Ga) was photographed under polarized light in order to make that structure visible. Each grain reflects light differently because the atoms in each grain are aligned in different directions. Efforts are under way to grow grains of plutonium with linear dimensions on the order of 1–10 mm.  
(Photo by Ramiro Pereyra)

discuss our purification techniques and crystal-growth program. We have already grown a plutonium grain that was large enough to be measured by photoemission spectroscopy.

## Techniques for Growing Plutonium Crystals

**Growing Crystals from Molten Plutonium.** The easiest way to obtain single crystals of a material is to grow them from the liquid phase (also called the melt). As the molten metal cools and solidifies, the atoms begin bonding



**Figure 2. The Low-Gallium Composition of the Plutonium-Gallium Binary Phase Diagram**

Pure plutonium has the most allotropes of any element. Following its phase transformations down the leftmost axis, we notice that liquid plutonium (L) solidifies into the  $\epsilon$ -phase below 640°C and then assumes five more structural phases ( $\delta'$ ,  $\delta$ ,  $\gamma$ ,  $\beta$ , and  $\alpha$ ) as it cools to room temperature. Alloying plutonium with small amounts of gallium (less than about 2.5 wt % gallium) reduces the number of allotropes from six to two. For example, at 1 wt % gallium (red line), the molten alloy cools by passing through a mixed (L +  $\epsilon$ )-phase, then a pure  $\epsilon$ -phase, then a mixed ( $\epsilon$  +  $\delta$ )-phase before reaching the  $\delta$ -phase, which is stable down to room temperature. The first bits of  $\epsilon$ -phase material to solidify from the (L +  $\epsilon$ )-phase have a higher gallium concentration than the melt. We determine the exact composition by following the first horizontal tie-line in the (L+ $\epsilon$ )-region to the right. Newly solidifying material has less gallium, and thus there are composition gradients within each grain (coring). Coring reoccurs when the alloy passes through the ( $\epsilon$  +  $\delta$ )-phase.

only two allotropes ( $\epsilon$  and  $\delta$ ), and the  $\delta$ -phase forms at approximately 500°C. This phase is then thermodynamically stable down to room temperature.

Moment produced several large grains by the Bridgeman technique: the melt froze and slowly transformed to the  $\delta$ -phase as it passed through a decreasing temperature gradient. (Moment recalls his work in the accompanying article beginning on page 233.) As revealed by x-ray pictures taken with a

back-reflection Laue camera, however, all those large grains contained substructure. They were therefore unsuitable for high-quality measurements of physical properties.

One reason for the low grain quality might have been the internal conditions resulting from coring. As discussed in Figure 2, when the alloy freezes from the melt or passes through a mixed phase, such as liquid and  $\epsilon$ , (L +  $\epsilon$ ), the grains that form have a higher concen-

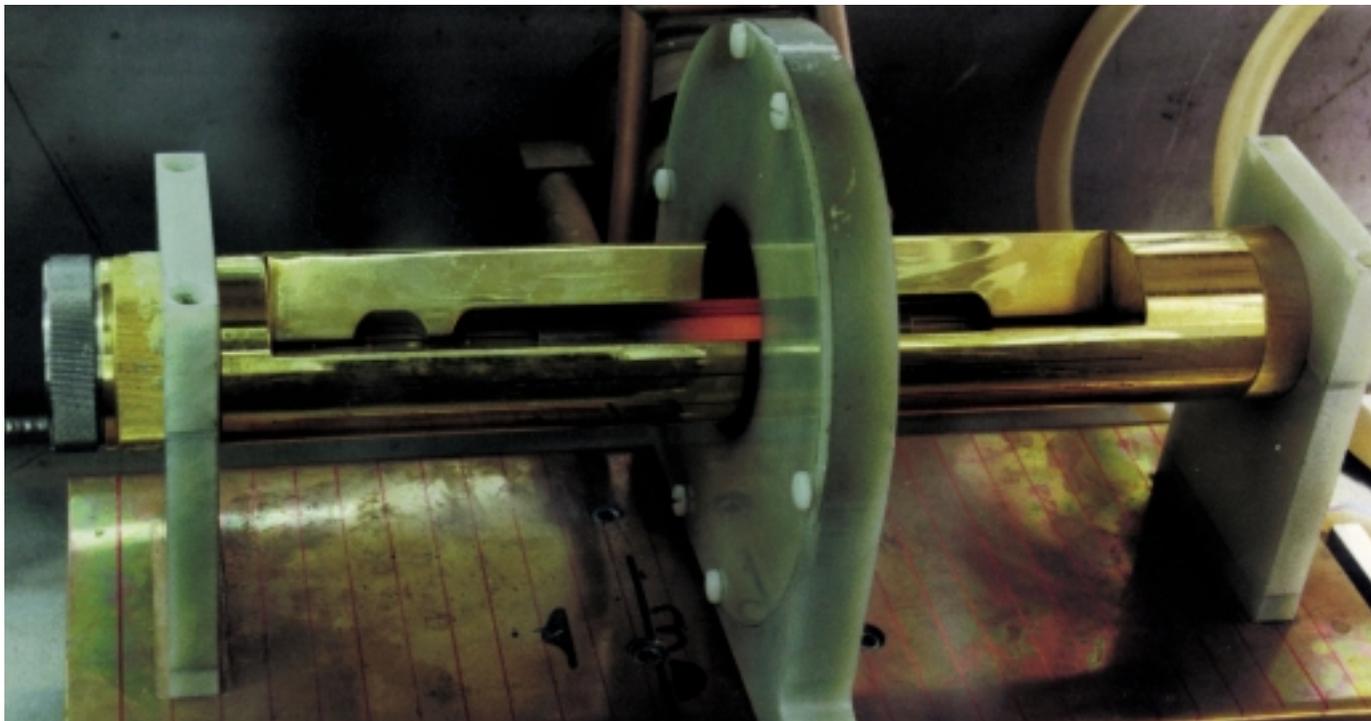
tration of gallium at the center. The uneven distribution of alloying material introduces strain into the crystal lattice that could detrimentally affect grain growth.

Primarily to avoid coring and other potential problems associated with the  $\epsilon$ - to  $\delta$ -phase transition, Moment abandoned the Bridgeman technique and focused his attention on growing plutonium grains by strain-anneal methods. Those methods ultimately proved to be successful, and his measurements of the elastic constant are still the only ones made on a single crystal of  $\delta$ -phase plutonium. Our current program has been guided by Moment's experiences.

**Growing Plutonium Crystals in the Solid State.** Strain-anneal techniques allow crystals to grow entirely within the solid state. During the strain-anneal process, the metal is plastically deformed so that dislocations form within it. The dislocations are disruptions to the minimum-energy state of the perfect lattice and are consequently a form of stored energy. At small plastic strain values (less than 10 percent), approximately 1 to 4 percent of the strain energy is stored within the lattice from dislocations, and the rest is dissipated as heat.

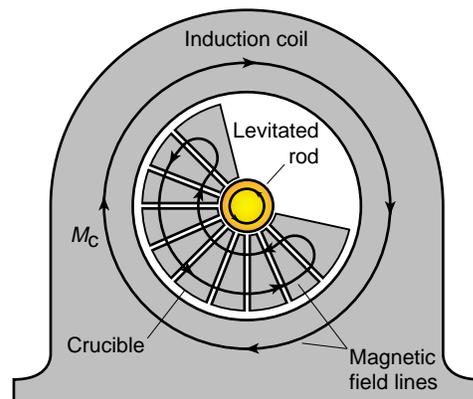
The stored energy is released when the metal is heated during the first step in the annealing process. The energy drives the formation of new grains in a process called recrystallization. Keeping the metal at constant high temperatures (the next step in the annealing process) then allows the recrystallized grains to grow larger through the migration of grain boundaries.

A grain boundary has a surface energy. Smaller grains have proportionally more surface energy than larger ones, so it is energetically favorable to merge smaller grains into larger ones. The boundary migrates as the atoms from one grain shift and become integrated into another. One grain is "consumed" while the other grows. In principle, one grain can dominate, growing steadily larger until the system reaches equilib-



**Figure 3. Levitation Zone-Refining Furnace**

An electromagnetic-levitation furnace consists of a crucible that holds the sample and an induction coil. As shown in the schematic on the right, radio-frequency power running through the coil induces currents to flow in the crucible. The current generates a magnetic field  $M_c$  that induces eddy currents to flow in the sample, which heats up and melts. But the eddy currents generate a secondary magnetic field in the direction opposite to  $M_c$ . Magnetic repulsion causes a zone of liquefied metal to levitate a small distance from the crucible walls. The photo shows a stainless steel rod loaded in the horizontal crucible. The glowing region under the induction coil is the levitated molten zone, and moving the crucible causes the zone to sweep through the rod. Elements that lower the melting point of the material travel with the zone, while those that raise the melting point diffuse into the solid. In either case, impurities are swept to the end of the rod, which are then cut off. For our program, we purify rods of  $\alpha$ -phase plutonium, rather than  $\delta$ -phase, to avoid complications stemming from the addition of gallium.



rium. Grain-boundary migration is enhanced at high temperature because the heat increases the mobility of the atoms. As mentioned earlier, specimens containing 1 wt % gallium can be annealed at temperatures as high as 500°C and still remain in the  $\delta$ -phase (refer to Figure 2.)

The strain-anneal technique is clearly advantageous for alloy systems and multiphase materials such as plutonium. Because the temperature is kept within the room-temperature stable phase, there are no phase transformations and no coring effects. Once a

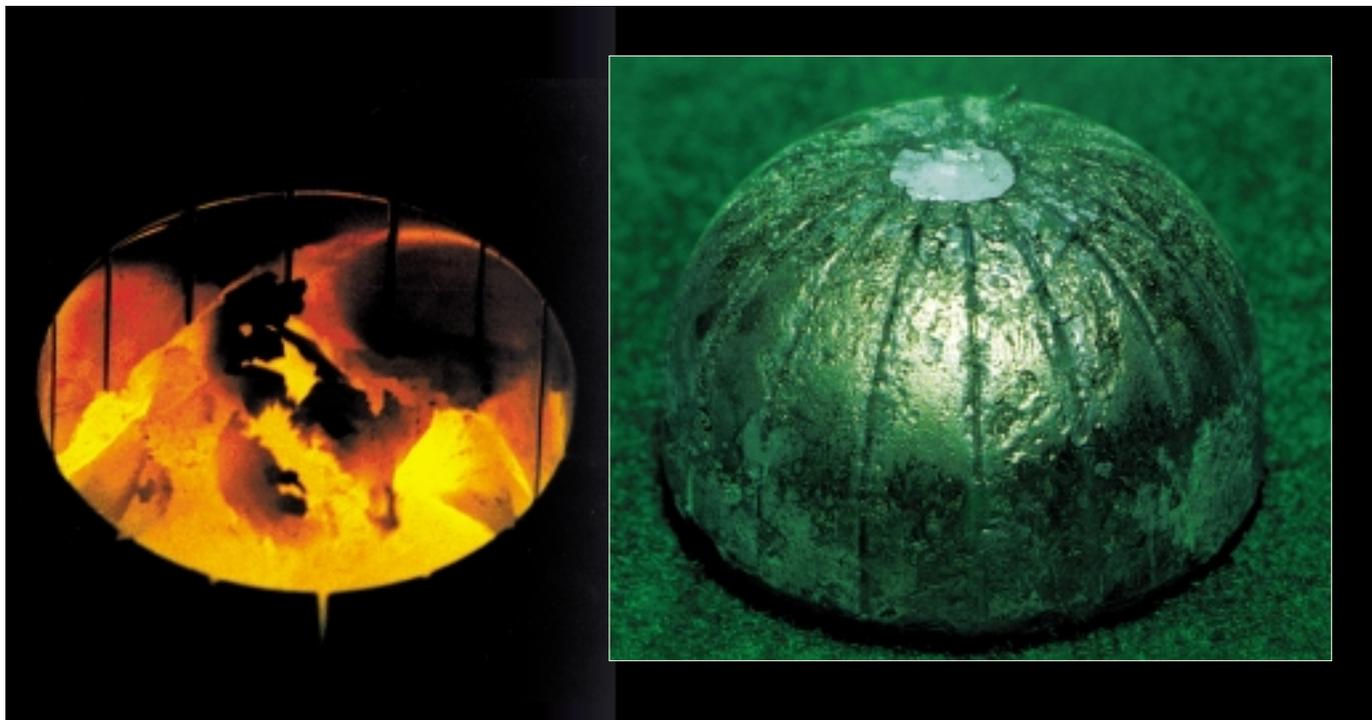
large grain forms, its structure can be preserved down to room temperature.

### Los Alamos Program for Growing Plutonium Crystals

**Purification.** Because impurities hamper the mobility of grain boundaries, any crystal-growth methodology hinges on starting with plutonium metal that is free of elemental impurities. Consequently, the first step in our program is to purify the plutonium starting material. Purification must be done on molten

plutonium, but the strong affinity that the liquid exhibits for almost all elements severely complicates the process. The elements that make up the container holding the liquid inevitably contaminate the melt.

We have solved this problem by using electromagnetic levitation furnaces. These devices, consisting of an induction coil and a crucible, are designed to levitate molten material. Any interactions between the crucible and the liquid metal are therefore eliminated. A levitation furnace is described in more detail in Figure 3. No other



**Figure 4. Vacuum Distillation of Plutonium Metal**

In the photo on the left, molten plutonium metal held suspended in the middle of a vertically-oriented crucible by an electromagnetic field. Americium and gas impurities boil off. Enough gallium has been added to stabilize the  $\delta$ -phase plutonium upon solidification. The photo on the right shows a half sphere of gallium-stabilized  $\delta$ -phase plutonium that was produced by vacuum distillation in a levitation furnace. The lines on the surface reveal where the plutonium solidified to the shape of the mold. Samples for growing crystals were fabricated from this specimen.

laboratory in the world uses such advanced equipment to purify plutonium.

Our purification technique starts with plutonium metal that has already been purified twice by electrorefining and has then been cast into a rod. We clean the rod's surface to get rid of any oxides and hydrides that may have formed. At this point, the metal typically contains impurity levels in

the range of 500 to 600 parts per million (ppm). Iron, uranium, magnesium, calcium, nickel, aluminum, potassium, and silicon are among the impurities.

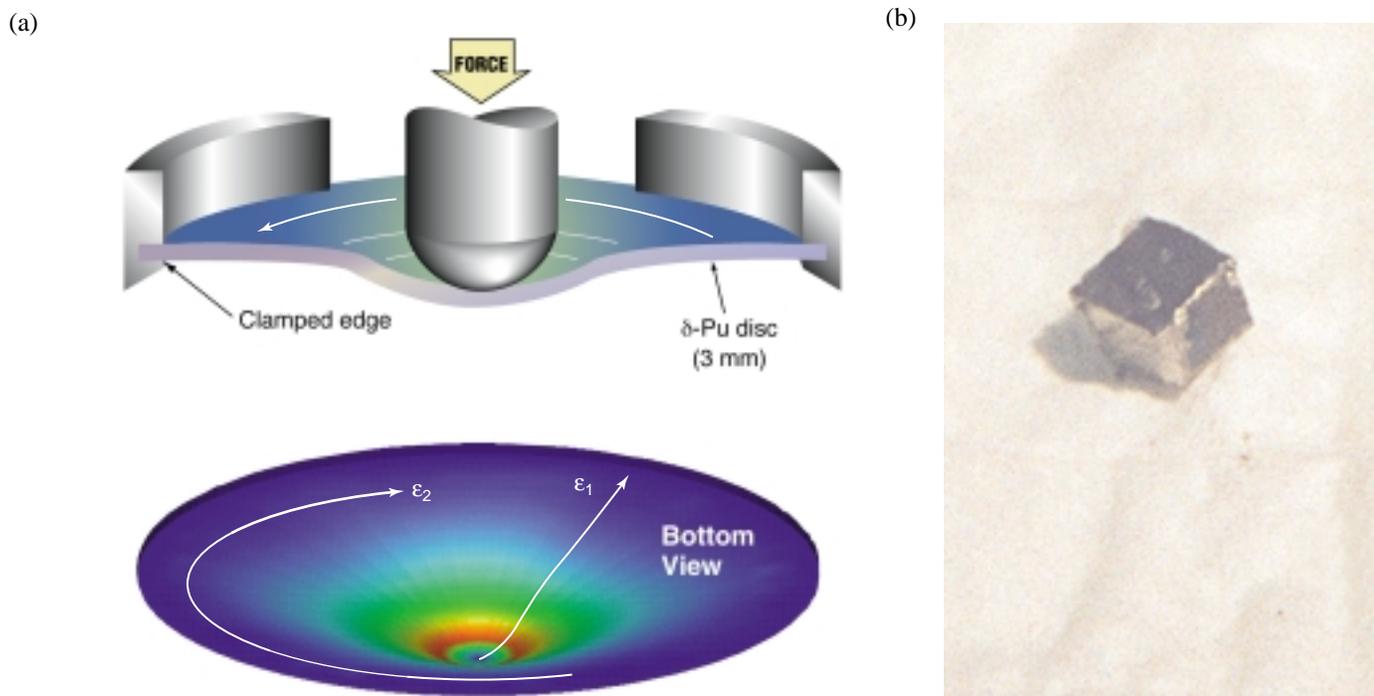
The rod is placed in the horizontal crucible of the levitation furnace, as shown in Figure 3. The induction coil of this furnace is the large disk in the middle of the photo. Only the small section of the rod directly under the induction coil is liquefied and levitated. When we move the crucible, the molten zone passes slowly through the rod in one direction. Impurities that lower the melting point of the metal remain in the liquid zone, whereas those that raise it are driven into the solid material. Because impurities either move with the zone or are pushed in front of it, both kinds are eventually swept to the end of the rod. Repeating this procedure several times leaves the central portion of the rod highly purified.

We use a mass spectrometer with very low detection limits to measure the impurity levels of 78 trace elements. Results to date indicate that zone refining in a levitation furnace reduces impurities from 523 to 174 ppm; uranium accounts for about

70 percent of that remainder.<sup>1</sup> Also, we have not detected any crucible material in our sample, which indicates a complete lack of plutonium-crucible interactions.

The purified rod then undergoes vacuum distillation in a vertical levitation furnace, a process that purges the rod of americium and interstitial gas impurities. The zone-refined plutonium is placed under reduced pressure ( $10^{-7}$  torr) in a cylindrical, vertical crucible. An induced high current circulates through the entire metal rod, which melts and levitates. Because americium and other impurities have a high vapor pressure, they distill away. We also add enough gallium during this stage to produce the plutonium-gallium alloy. Sudden removal of furnace power lets the molten alloy drop into a chilled copper crucible, where it quickly solidifies. (See Figure 4.) Because the solidification is so rapid, coring is

<sup>1</sup>Previously, researchers could only report on the impurity levels of 20 to 40 trace elements because their measurement techniques had higher detection limits. Although our material is likely the purest that has ever been produced, our total impurity levels are often higher than the levels reported in the early literature.



minimized, and we obtain an as-cast density of 15.938 grams per cubic centimeter ( $\text{g}/\text{cm}^3$ ), which is only slightly higher than the theoretical  $\delta$ -phase density of 15.810  $\text{g}/\text{cm}^3$ . (A small amount of coring creates some high-density  $\alpha$ -phase plutonium that increases the overall density.)

Recent results obtained from vacuum distillation show that the americium could be removed almost entirely. Several weeks after distillation, the measured impurity level was  $1.5 \pm 0.3$  ppm. During that time, however, some of the plutonium-241 that was present in the starting material decayed to americium-241. What we detected was simply the newly created americium.

The ability to make plutonium samples that are essentially free of americium is critically important to the Laboratory. Such a sample is needed for an experiment to measure the  $(n,2n)$  cross section of plutonium-239. The cross section can be used to infer the neutron spectrum in an exploding weapon and is therefore a central concern of the Science-Based Stockpile Stewardship program.

Using ultrapurified material, we set up a series of experiments to grow

large grains of  $\delta$ -phase plutonium. Our starting material was a set of 3-milli-meter-thick polycrystalline disks (1 wt % gallium) that had been cut from a homogenized ingot (average grain size of 30 micrometers). After rigidly fixing each disk's circumference into a die, we deformed the disks over a hemispherical punch at room temperature, as in Figure 5(a).

This setup made it easy to strain the material uniformly in both the radial and circumferential directions (balanced-biaxial strain). The total, true strain on the surface is described by the three diagonal components of the true strain tensor: the radial component ( $\epsilon_1$ ), a circumferential component ( $\epsilon_2$ ), and a through-thickness component ( $\epsilon_3$ ). Only two of those components are independent. The strain peaks at the pole and goes to zero at the periphery. Because the volume of the material is conserved, the disk also becomes thinner. At small plastic deformations, a uniform through-thickness compressive strain is also achieved that varies with the radius.

With the strain-anneal technique, the largest grains are produced if the metal is strained a "critical" amount and then annealed. (See Figure 2 on page 235 in

#### Figure 5. Biaxial Strain in a Plutonium Disk

(a) A 3-mm-thick disk of gallium-stabilized  $\delta$ -phase plutonium is stretched in two dimensions with a hemispherical punch. The magnitude of the strain decreases in the radial direction, from the pole to the edge. A strain gradient, described by  $\epsilon_1$  is therefore generated and is shown here by different bands of color. A second strain gradient is produced as the disk becomes thinner. (b) After having been annealed isothermally at 480°C for 90 hours, the disk contained several newly grown, large (1 mm) plutonium grains. The cube shown above contains one of those grains. Some of its electronic-structure properties were later measured by photo-emission spectroscopy.

the article "A Single-Crystal Saga.") If strained too little, the metal does not acquire enough dislocations (that is, stored energy) to promote recrystallization, but if strained too much, it acquires so many dislocations that grain refinement occurs. We wanted to achieve this critical strain at the center of the disk so that the grain would then

grow out uniformly in all directions. Unfortunately, the critical strain depends on many factors, including the initial sizes and orientations of the grains and the manner in which the load is applied to the bulk material. That is why the critical strain can be determined only empirically for each type of sample.

After a 90-hour isothermal anneal at 480°C and reduced pressure, grains of 1-2 millimeters in length were produced. The largest grain was located about 6 mm from the center of the disk. We estimated a critical strain of about 3 percent. Analysis of the disc surface at the location of the largest grain yielded components of the strain tensor (corresponding to the critical strain for this material) of  $\epsilon_1 = 0.022$  and  $\epsilon_2 = 0.018$ .

Having some sufficiently large grains available to us, we extracted from the disk a small section containing one such grain—see Figure 5(b). That crystallite was measured by photoemission spectroscopy, as discussed in the article “Photoelectron Spectroscopy of  $\alpha$ - and  $\delta$ -Plutonium” on page 168.

We have also experimented with a second method for growing crystals. Liquid plutonium-gallium alloy is dropped out of the magnetic field of a levitation furnace and is chill-cast in a mold shaped like a long, thin cone. The microstructure of this chill-cast plutonium consists of very fine, small acicular (or needlelike) grains  $10 \times 25$  micrometers in size.

We anticipate that the conical geometry of this chill-cast sample and the fine grain size will help promote grain growth. Because the tip of the cone is so small, the number of grains competing to grow there is reduced. Hopefully, a single grain will grow at the expense of the others once we begin a strain-anneal process. Because the grain size in the rest of the sample is so small, there is a lot of surface energy available to help drive that grain growth, and the growing “seed” grain could continue to expand into the cone. Ideally, the large volume at

the top of the cone would consist of a single grain from which precisely oriented samples could readily be cut.

The lack of large single crystals is currently the only obstacle that prevents researchers from obtaining high-quality data on the fundamental solid-state properties of  $\delta$ -phase plutonium. By applying several variations of the strain-anneal technique to  $\delta$ -phase plutonium, we have enjoyed some success in growing millimeter-sized grains. Our future work is aimed at developing crystal-growing methods with repeatable results. ■

### Acknowledgments

The authors thank Michael Stout, David Embury, Manuel Lovato, Ramiro Pereyra, Jim Smith, Larry Thulen, Jason Cooley, and Karl Staudhammer of the Materials Science Division. Special thanks to Floyd Rodriguez, Fred Hampel, and Kenny Vigil for laboratory assistance, and to Mick Greenback and Larry Vaughn for photography and induction support, respectively.

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