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The Elastic Properties of Plutonium in the BCC Epsilon Phase

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ABSTRACT

The ultrasonic resonance method was used to determine the elastic constants of polycrystalline plutonium up to its melting point. Special attention was devoted to the ε phase, and its Poisson ratio ($\sigma \approx 0.2 \pm 0.02$) up to 520°C, its Young's modulus ($E = 1106 \times 10^7$ N/m^2 at 430°C), and the temperature coefficient of the modulus ($dE/dT = (-0.40 \pm 0.03)\ 10^8$ N/m^2°C) are determined. From these values the compressibility is deduced and compared with a theoretical value calculated from a new expression for Grüneisen's constant; further conclusions are drawn concerning the diffusion mechanism in this bcc phase.

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1. INTRODUCTION

The elastic constants of the high-temperature ε phase of plutonium are the least known of those of all phases. This is due principally to the difficulties in applying, in a glove box, classical methods to a high-temperature phase whose mechanical properties are poor.[1,2] We proposed to determine for this phase Young's modulus, E, and its temperature coefficient; Poisson's ratio, σ; and the compressibility, as much to fill this gap as to contribute supplemental information to the determination of the mechanism of atomic diffusion in this phase, recently christened "abnormal."[3]

2. EXPERIMENTAL METHODS

We could not devise a direct static method, such as tracing *stress-deformation curves* in tension, compression, or torsion, to determine the elastic constants of ε-phase plutonium in its stability region (475-640°C) because, *at these temperatures*, the observations may be masked or falsified by the effects of creep.[2] A hydrostatic, high-pressure apparatus of the type used to study atomic diffusion under pressure in the ε phase[4] could, after modification, serve for the elastic constant studies. However, the measurement precision anticipated from the quasi-hydrostaticity of the pressure and the supposed high compressibility of the ε phase certainly would be counterbalanced by errors due to deformation of the apparatus under pressure and high temperature, to uncertainty in the compressibility of the pressure transmitter (pyrophyllite) at these temperatures, and to the reduced size of the ε-phase field under pressure.[5,6] There remain only the dynamic ultrasonic methods, employed with success by Kay and Linford[1] and by Lallement[7] for the lower temperature phases but difficult to use at and above the γ → δ transition because of the large signal attenuation.[1,8]

The sample is heated by radiation, under high vacuum, in a furnace placed in a glove box with an argon atmosphere. The furnace, formed from a Crusilite (bonded SiC) resistor, is centered in a water-cooled cylindrical chamber and protected by two molybdenum shields. Any of a wide choice of heating rates is easily attainable through use of a variable autotransformer connected to the shaft of a geared motor. Because of the thermal inertia of the furnace, regulation of the temperature by an "on-off" controller is satisfactory. The general arrangement of the installation is given in Fig. 1.

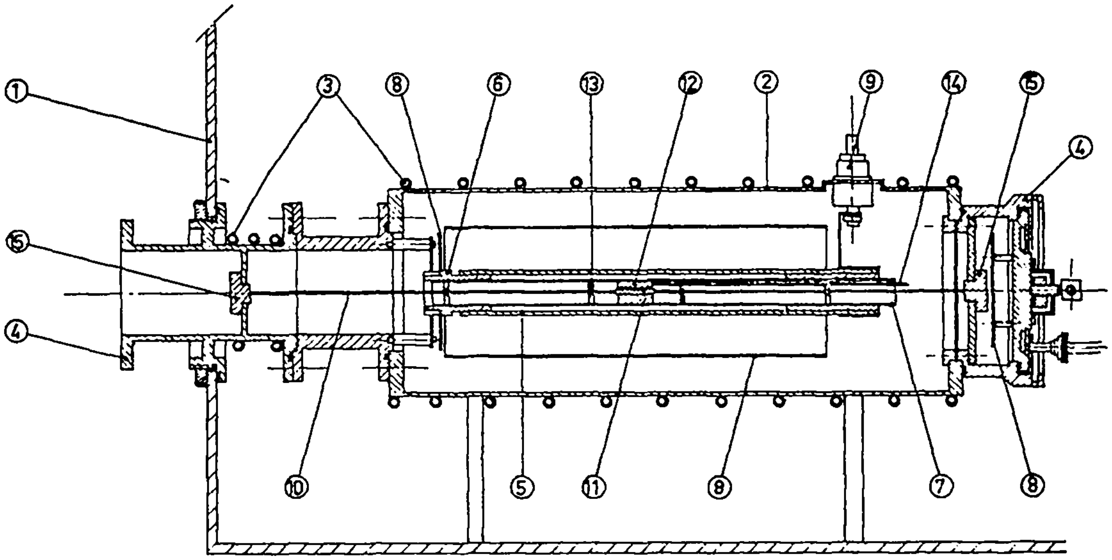

Fig. 1a. Apparatus for the study of the elastic properties of plutonium by the ultrasonic resonance method.

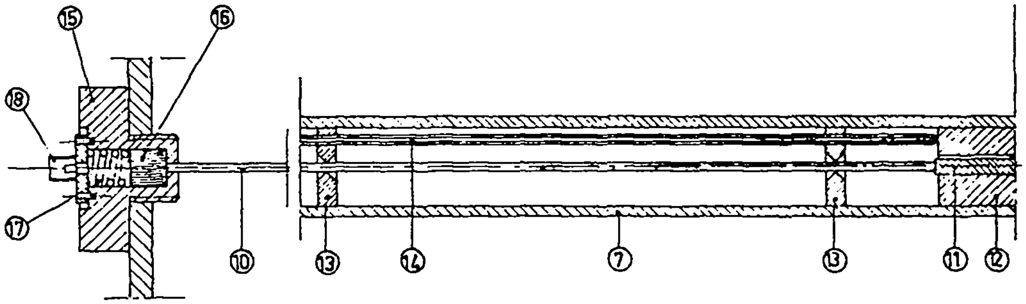

Fig. 1b. Half-scale detail of the vibratory system.

1. Glovebox wall
2. Furnace chamber
3. Cooling circuit
4. Vacuum sealed opening
5. Crusilite furnace resistor
6. Insulating collar
7. Stainless steel tube
8. Thermal shielding
9. Current lead-in
10. Alumina rod
11. Sample
12. Pyrophyllite sample holder
13. Pyrophyllite supports
14. Thermocouple
15. Quartz holder
16. Electrostrictive ceramic
17. Compensating spring
18. Signal input or output (coaxial cable)

Longitudinal, transverse, or torsional vibrations can be generated in the sample by means of disks of electrostrictive ceramic (Ø = 10 mm, e = 10 mm) through an alumina rod (suitably positioned along the sample axis), which permits placing the electrostrictor outside the furnace and near the wall of the vacuum chamber. The ceramic, a mixture of lead zirconate and titanate with rare-earth oxides added, exhibits ferroelectric characteristics only below 319°C. An analog device receives the mechanical vibrations from the sample and transforms them into electrical impulses which, amplified, sweep the vertical field of an oscilloscope while the input impulse sweeps the horizontal field, so that a Lissajous ellipse is formed. The slope of the major axis with respect to the horizontal provides a rough determination of the propagation rate of the ultrasonic waves, but the sharp maximum (monitored on a millivoltmeter after rectification of the signal) of the length of the minor axis at resonance provides a precise determination of the resonant frequency and its harmonics.

The samples of plutonium, for which analyses are given in Table I, are cast and machined cylinders, 4-mm diam and 40-mm long (at room temperature). The temperature is measured by a Chromel-Alumel thermocouple slightly offset in relation to the sample, but positioned, like the sample, in the zone of minimum temperature gradient within a stainless steel protection tube. The sample rests in a pyrophyllite holder, which no doubt increases the number of parasitic resonant frequencies and increases the risk of masking weak phenomena[1] but which does prevent creep of the plutonium by gravity. Creep occurred at as low as 450°C in a preliminary trial in which the sample was supported at its extremities (vibration nodes) by two thin pyrophyllite rings.

Although the alumina rods were much longer than the sample, it is difficult to extract the resonant frequency of the sample from the accompanying parasitic frequencies. In practice, Young's modulus is determined at ordinary temperatures by the echo, rather than the resonance, method. One sends high-frequency pulses into the sample (to minimize the absorption in the sample) with the aid of a piezoelectric quartz crystal and collects these pulses, as well as those reflected several times from the opposite face of the sample, on the receiving crystal. The successive echoes are registered on the oscilloscope screen, and, by using the time base of this device, one calculates the propagation velocities, V_1 and V_2, of the longitudinal and transverse waves. (Quartz crystals of different cuts should be used for each of these two determinations.) Young's modulus, E, is calculated by the formula:

$$E = 4\rho \ (3/4 \ V_1^2 - V_t^2) / \left\{ (V_1/V_t)^2 - 1 \right\} \quad , \qquad (1)$$

where ρ is the density of the material.

The fundamental frequency,

$$f_1 = (2\ell)^{-1} (E/\rho)^{1/2} \quad , \qquad (2)$$

thus separated from the spectrum of parasitic frequencies is then followed continuously as a function of temperature by exciting resonance in the sample. It is, in effect, impossible to use the echo method at higher temperatures because the quartz in contact with the sample deteriorates rapidly. Note that recording of all resonant frequencies that appear, as well as those that disappear, at phase changes constitutes a laborious but sure method of determining the proper harmonics for each plutonium phase.

The sample is heated slowly and kept at the experimental temperature long enough to attain equilibrium. Young's modulus at all temperatures

TABLE I

SPECTROGRAPHIC ANALYSIS OF THE PLUTONIUM USED

		Impurities Determined (ppm)														
Sample	Density	Ag	Al	B	Cr	Cu	Fe	Mn	Mg	Mo	Ni	Pb	Si	Sn	Zn	Total*
1	19.43	10	10	<0.5	<5	12	7	1	52	<10	5	3	82	6	15	~ 220
2	18.72	2	<10	<1	23	16	65	20	19	<10	85	60	24	7	300 << 1000	~ 1000

*For the 14 impurities determined.

is calculated by Eq. (2) which is preferably written as follows to take account of the length and density modifications in the heated sample.

$$E = 4\rho_0 \ell_0^2 f_1^2 r_0/r, \qquad (3)$$

where the subscript 0 refers to dimensions measured at ordinary temperatures and r is the radius at temperature T of the plutonium atom, as compared to a sphere whose volume is that of the lattice divided by the number of atoms it contains. We will not take into account errors in evaluating the resonant frequency or in the measurement of length, ℓ_0, and density, ρ_0 (obtained by a hydrostatic method). ε-phase plutonium, especially, exhibits an uncontrollable deformation of the sample cross section in contact with the alumina rods, although weak springs at the ends of the vibratory assembly absorb some of the dimensional variation of the alumina and the sample during a thermal cycle. One may assume that $\Delta E/E = 0.01$.

3. RESULTS

The curves of Young's modulus as a function of temperature for two samples of different densities, Fig. 2, not only contribute some new results for the δ, δ', and ε phases (Table II), but also permit comparison with values already published for the phases at lower temperatures.[1,7] In the α and γ phases, the temperature coefficient is seen to be smaller than that given by others.[1] As in the case of uranium,[9,10] and as noted by Kay and Linford,[1] the ultrasonic methods give larger values than do the direct methods,[11] and Young's modulus at a given temperature increases with density. Certain transitions are completely masked, in particular, the β → γ phase change, for which some authors[1,11] have noted an increase in the crystalline cohesion. In the δ phase, Young's modulus agrees well with that determined by extrapolation of results obtained on Pu-Al and Pu-Ce alloys (1.4 x 10^{10} N/m^2 at 420°C).[8] The mechanical properties of ε-phase plutonium are particularly poor, the Young's modulus being ten

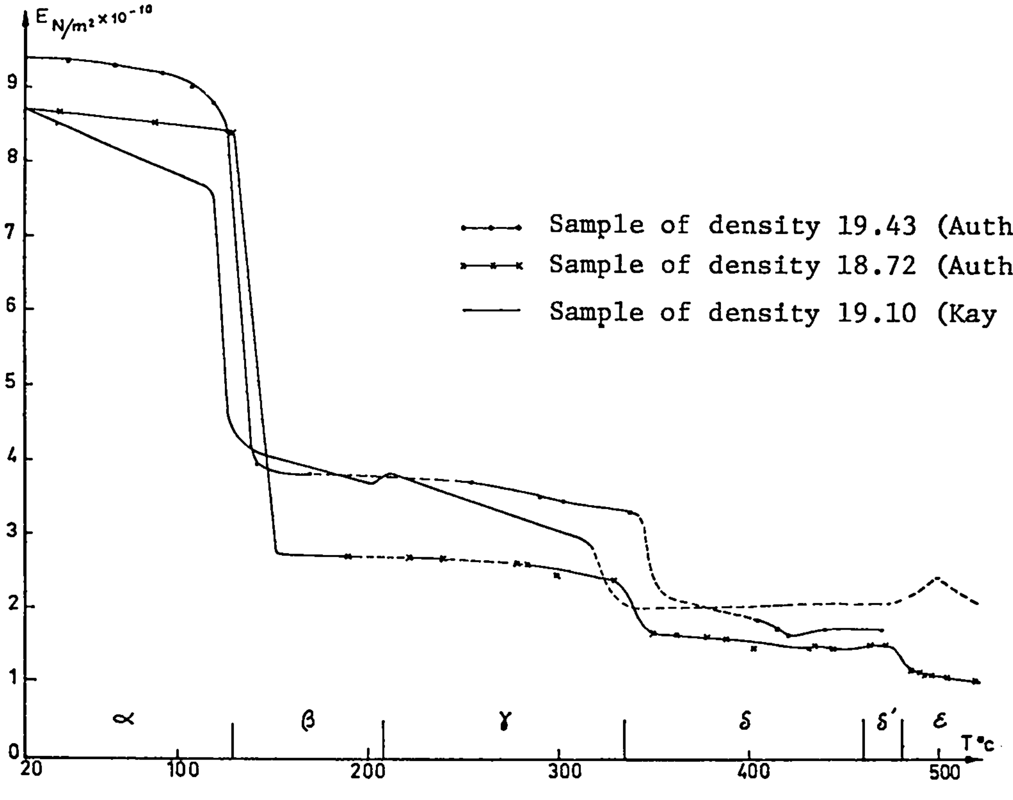

Fig. 2. Young's modulus of plutonium up to 520°C.

TABLE II

YOUNG'S MODULUS OF PLUTONIUM IN δ, δ', AND ε PHASES

Phase	δ									δ'		ε					
T (°C)	350	362	378	388	402	414	420	432	444	464	472	485	490	492	496	504	520
E_I* ($10^7 N/m^2$)					1810	1700	1680		1700		1680						
E_{II}* ($10^7 N/m^2$)	1635	1630	1590	1580	1460			1478	1440	1478	1460	1115	1106	1070	1060	1055	970

*Sample of density 19.43 at T = 30°C.
*Sample of density 19.10 at T = 30°C.

times smaller than that for the α phase. The temperature coefficient,

$$dE/dT = (-0.40 \pm 0.03)10^8 N/m^2\cdot{}^\circ C,$$

agrees well with the theoretical value,

$$dE/dT = (-0.47 \pm 0.03)10^8 N/m^2\cdot{}^\circ C,$$

deduced from Dupuy's results for self-diffusion in the ε phase[3] and from those of Nelson and his coworkers[12] for linear creep in that phase, obtained by means of the equation proposed by Sherby,[13]

$$\Delta H_{creep} = \Delta H - (nR_0T^2/E)dE/dT, \qquad (4)$$

where ΔH_{creep} = activation energy for linear creep, R_0 = the gas constant, and n = a constant equal to about 5.

Only two or three harmonics of the fundamental frequency are detectable. Their frequencies, given by[14]

$$f_i = (\tfrac{1}{2}i/\ell)(E/\rho)^{\frac{1}{2}} \left\{1 - (\tfrac{1}{4}\pi^2\sigma^2R^2i^2/\ell^2)\right\} \quad , \quad (5)$$

permit a graphical approximation of Poisson's ratio for the ε phase. At 485°C,

$$\sigma = 0.20 \pm 0.02 \quad ,$$

a value approaching those obtained for the lower temperature phases of plutonium.[1,7,15] Consequently, at this temperature, the modulus of rigidity of the supposed isotropic ε phase is

$$\mu = \tfrac{1}{2}E/(1 + \sigma = (4.65 \pm 0.15)\ 10^9\ N/m^2 \quad ,$$

and the compressibility is

$$\chi = 3\ (1 - 2\sigma)/E = (16 \pm 1.5)\ 10^{-11}\ m^2/N.$$

This enormous compressibility explains the experimental difficulties --creep, sample deformation, and signal absorption-- encountered during this study. The compressibility is comparable to that of a very soft metal such as sodium or potassium or to that of a liquid such as ether,[16] and it reflects the relationship that seems to exist between ε-phase plutonium and its liquid, i.e., small heat of fusion, similar densities and atomic radii, and large diffusion coefficients in the ε phase:

$$1.2 \times 10^{-7} cm^2/s \text{ at } 500^\circ C.^3$$

It is possible to obtain a theoretical value of the compressibility, χ, for the ε phase from the simplified expression for the Grüneisen constant, Γ, not taking rigorously into account the electronic specific heat, certainly large for plutonium:

$$\Gamma = \alpha V/(\chi C_v) = -(\partial \log \nu_0/\partial \log V) \quad , \qquad (6)$$

where

α = coefficient of volumetric expansion,
V = volume of the gram atom,
C_v = specific heat at constant volume,

and

ν_0 = Debye temperature (cutoff frequency of the Debye spectrum).

Lindemann's law,[17]

$$\nu_0 = C\left\{T_f/(MV^{2/3})\right\}^{1/2} \quad , \qquad (7)$$

where

T_f = temperature of fusion of the phase,
M = molar volume,
and
C = a constant,

permits development of a new expression for the Grüneisen constant,[18,19]

$$\Gamma = \frac{1}{3} + \frac{1}{2}\chi\ (\partial \log T_f/\partial P) \quad . \qquad (8)$$

In comparison with Eq. (6), it gives

$$\chi = 3\left(\frac{\alpha V}{C_v} - \frac{1}{2}\,\frac{\partial \log T_f}{\partial P}\right) \quad . \qquad (9)$$

The slope of the liquidus in the plutonium phase diagram, taken from Stephens[5] and recently confirmed,[20] is such that

$$\partial \log T_f/\partial P = -4.82 \times 10^{-6}/\text{bar}.$$

As we have pointed out in another connection,[18] taking into account the experimental difficulties inherent in studies of plutonium at high pressures, this result agrees well with the Clausius-Clapeyron equation,

$$\partial \log T_f/\partial P = \Delta V_f/\Delta H_f = -5.49 \times 10^{-6}/\text{bar},$$

where

ΔH_f = 693 cal/mole (enthalpy of fusion),[21]

and

$\Delta V_f = -0.159$ cm^3 (taking the density of liquid plutonium at 665°C as 16.50 and the coefficient of expansion at the same temperature as 50×10^{-6}).[22]

Application of Eq. (9) to the case of ε-phase plutonium gives, then, at 485°C,

$$\chi = 23 \times 10^{-11}\ \text{m}^2/\text{N} \quad .$$

The agreement with experiment is satisfactory, given the inexactness of the theoretical formula, and it appears that the enormous compressibility of ε-phase plutonium is directly related to the fact that its density is less than that of the liquid phase.

4. CONSEQUENCE.
THE COMPRESSIBILITY AND ACTIVATION VOLUME FOR SELF-DIFFUSION

The activation volume for diffusion, i.e., the change in volume of the crystal during a diffusion jump, is given for an isotropic cubic crystal by the equation,[23]

$$\Delta V = -RT\ \left[(\partial \log D/\partial p)_T + \chi_T(\tfrac{2}{3} - \Gamma)\right] \quad ,$$

where D is the coefficient of diffusion at pressure p. We have undertaken the study of self-diffusion of ε-phase plutonium under pressure. The few experimental results obtained to date seem to indicate that the self-diffusion coefficient increases exponentially with pressure, which is quite unusual.[18] Because of the great compressibility of ε-phase plutonium and the small Grüneisen constant ($\Gamma = 0.23$ at 537°C), the term $-RT\chi_T(\frac{2}{3} - \Gamma)$, generally neglected in comparison with the first term in the expression for the activation volume, is negative here and represents about 4% of the volume of the gram atom; that is, it agrees with the increase of the self-diffusion coefficient under pressure to give a distinctly negative activation volume (and of the order of 42% of the molar volume at 537°C). It is interesting to compare the size and sign of this value with those that one can obtain from the existing theories.

Rice and Nachtrieb,[24] in remarking that the self-diffusion coefficient at a given pressure and temperature depends only on the ratio $T_f(p)/T$, where $T_f(p)$ is the temperature of fusion at pressure p, show that one can write

$$\Delta V = \Delta H(\partial \log T_f/\partial P) - RT\chi_T\ (\tfrac{2}{3} - \Gamma) \quad ,$$

where $\Delta H = 18.5 \pm 2.5$ kcal/mole,[3] the activation enthalpy for self-diffusion. Application of this formula to ε-phase plutonium gives, at 537°C, $\Delta V = -33\%$ of the molar volume.

It seems that "ring mechanism" diffusion should no longer be considered for body-centered cubic metals and alloys,[25,26] but it is interesting to note that Zener's theory[27] also leads to a negative activation volume for ε-phase plutonium. We recall that Zener assumed that the twisting of the lattice (due, on the atomic scale, to the diffusion mechanism) could be represented, on the macroscopic scale, by the twisting of a cylindrical bar subjected to a couple applied to its end surfaces. This leads to the expression

$$\Delta V = 2\Delta G\chi(\Gamma - \frac{1}{3}) \quad ,$$

where the free energy of activation,

$$\Delta G = \Delta H - RT \log \left\{D_0/(fa^2\nu)\right\} \quad ,$$

can be calculated easily from Dupuy's results[3] for the activation enthalpy, ΔH, and the frequency factor, D_0. f is the correlation factor, and ν can be calculated using Lindemann's law,[17] which relates the Debye frequency and the melting temperature of the metal. One finds that at 537°C, $\Delta V \simeq -16.5\%$ of the molar volume.

Consequently, theory does not repudiate the few experimental results we have obtained; in any case, it confirms the negative sign of the activation volume. Thus, one can ask if it is still appropriate to consider a monovacancy diffusion mechanism in the body-centered cubic phase of plutonium inasmuch as the free energy of activation for self-diffusion[3] is very much smaller than that given by Gibbs' empirical rule for this diffusion mechanism in bcc structures,[28]

$$(\Delta G)_{T_f} \simeq 22.6\ T_f ,$$

and it is difficult to imagine an atomic model with this mechanism which takes into account the negative sign of ΔV. If the activation volume for the formation of a vacancy can be small because of general appreciable relaxation of the atoms surrounding a vacancy, the activation volume for its migration cannot be negative.

Shewmon and Aaronson[29] have shown, however, that these two features can be characteristic of a vacancy diffusion mechanism in body-centered cubic metals if they transform to a denser phase at lower temperature, as, for example, β-phase titanium, β-phase zirconium, γ-phase hafnium, and γ-phase uranium. One can then be tempted to explain in this fashion the diffusion anomalies of ε-phase plutonium, which transforms at 480°C to a face-centered tetragonal phase closely related to a face-centered cubic structure. Still, to verify the principal hypotheses of the theory, one must know that the elastic constant, $\frac{1}{2}(C_{11} - C_{12})$, increases as a function of temperature in the vicinity of the transition temperature[30] and that it is much larger than the constant C_{44}.[31] It would thus be necessary to prepare single crystals of ε phase stabilized to ordinary temperatures, which, in view of the current state of knowledge of plutonium, does not seem possible.

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