Photostatic Price $ [illegible]

Microfilm Price $ .80

Available from the
Office of Technical Services
Department of Commerce
Washington 25, D. C.

UCRL-7172

C.1

UNIVERSITY OF CALIFORNIA
Lawrence Radiation Laboratory
Livermore, California

Contract No. W-7405-eng-48

This paper was submitted for publication in the open literature at least 6 months prior to the issuance date of this Microcard. Since the U.S.A.E.C. has no evidence that it has been published, the paper is being distributed in Microcard form as a preprint.

THE PHASE DIAGRAM OF PLUTONIUM

D. R. Stephens

February 8, 1963

THE PHASE DIAGRAM OF PLUTONIUM

D. R. Stephens

Lawrence Radiation Laboratory, University of California

Livermore, California

February 8, 1963

ABSTRACT

The pressure dependence of the phase transitions of plutonium, including melting, has been measured to 35 kilobars. The phase transitions were detected by differential thermal analysis and by volume discontinuity. Three triple points were detected, the γ-δ-ϵ, γ-ϵ-liquid, and β-γ-liquid. The technique was not sufficiently sensitive to detect the δ-δ' transition, and thus the γ-δ-δ' triple point was not determined.

THE PHASE DIAGRAM OF PLUTONIUM

D. R. Stephens

Lawrence Radiation Laboratory, University of California

Livermore, California

February 8, 1963

INTRODUCTION

Plutonium is a very interesting element, not only due to its nuclear properties, but also due to its large number of polymorphic transitions. Thus, in spite of its hazardous nature, a great deal of work has been done on its physical properties. Several excellent reviews of the literature are available.[1,2,3] As a result of this previous work, the one-atmosphere phases are well known. Solid plutonium exists in six phases, designated α, β, γ, δ, δ', and ϵ. The transformation temperatures suggested by Wilkinson[1] are shown in Table 1. The crystal structures of the phases are known and have been summarized by Zachariasen.[4]

Table 1. One-atmosphere transition temperatures of plutonium

Transition	Temperature, °C
α-β	119 ± 2
β-γ	206 ± 3
γ-δ	319 ± 5
δ-δ'	451 ± 9
δ'-ϵ	476 ± 5
ϵ-liquid	639.5 ± 2

The α-β transition has been studied at high pressure by two previous investigators. Bridgman[5] studied the α-β transition to 7000 kg/cm^2 and also measured the room-temperature compressibility of Pu to 100,000 kg/cm^2. McWhan et al.[6] measured the α-β transition to 18 kilobars.* The object of the present work was to extend the study of plutonium phase transitions at high pressures to the other transitions, including melting.

EXPERIMENTAL METHOD

Most of the data were obtained by differential thermal analysis (DTA). Some data at lower pressures were obtained by volume discontinuity.

Differential Thermal Analysis (DTA)

Figure 1 shows the apparatus used for DTA runs. The high pressure die consisted of a tungsten carbide core and a hardened steel support ring. The die bore was 0.5005 inch to admit the 0.500-inch tungsten carbide piston. The sample assembly is similar to that used by Boyd and England[7] and Kennedy and Newton[8], thus it will be only briefly described. A graphite furnace, insulated from the sample by boron nitride, was used to provide internal heat. The plutonium sample, 0.095 inch in diameter by 0.125 inch long, was enclosed in a tantalum capsule which was in contact with the Chromel P and Alumel DTA thermocouple. Talc was used to insulate the furnace from the die and to act as the pressure transmitting medium. The talc cylinder was wrapped with lead foil to reduce friction. Closure of the die was effected by a stainless steel power lead with a 1/16-inch hole to admit

---

* 1 atm = 1.013 bar = 1.033 kg/cm^2. The kilobar is now the standard unit for high pressure research.

the thermocouple and insulation. The power lead was insulated from the die with a pyrophyllite sleeve.

The thermocouple and DTA signals were recorded by a Brown X_1, X_2 double-pen recorder. The working parts of the press were contained in a glove box maintained under an argon atmosphere so that the plutonium and high pressure components were completely contained in an inert atmosphere. The assembly of the sample and components was also done in this box.

In taking data, the sample was kept at constant pressure while the temperature was raised smoothly until a transition was detected. Then the heat was discontinued. Actually, the pressure rises slightly during heating, but this effect was small and was easily corrected.

The next step was to determine any necessary corrections to the indicated pressure due to the heating cycle. A hysteresis loop at room temperature of piston displacement versus pressure was obtained, using displacement gauges accurate to ±0.0001 inch. This established the friction, as described by Bridgman[9], and thus the true displacement versus pressure was determined for the sample assemblies at room temperature. Essentially the friction was taken as one-half the difference in pressure at constant displacement of the ascending and descending loops. The "backlash" of the initial portion of the descending loop was neglected.

Then displacement was measured at constant pressure for the sample assemblies undergoing the same heating cycle as for a run. The displacement for a given maximum temperature, such as 500°C, was noted for several pressures. Displacement-versus-pressure curves were thus obtained for maximum temperatures of 100, 300, 500, and 700°C. These curves, corrected for friction, were compared with the true curve obtained at room temperature. It was assumed that the two curves should match and that if they

did not, pressure corrections were necessary. It was found that the corrections were negligible. The effect of rapid internal heating was small, at least to 700°C. The expansion of the sample assembly showed up as effectively raising the pressure in the die.

Volume Discontinuity

Figure 2 shows the die used for volume discontinuity measurements. The diameters of the samples were similar to those for DTA; the bore of the die was 0.105 inch. The samples were not enclosed in any matrix for these runs. The die was made of Vascoloy Supreme steel, RC 48, with a Mo liner. Mo rings and wafers were used to contain the plutonium and to isolate it from the tungsten carbide piston. Thus only Mo was in contact with plutonium. The die was externally heated by a resistance winding. A plot of temperature versus displacement was obtained on an XY recorder. The temperature was measured with a Chromel P and Alumel thermocouple, and the displacement with a linear differential transformer. A transition was noted as a break in the slope of the curve, not as a clean discontinuity, so that the actual magnitude of the volume change was not obtained. This apparatus was calibrated similarly to the DTA and was used only for lower pressure data.

Data Reduction

The temperatures quoted were not corrected for any pressure effect. The effects are not known at present for the pressure-temperature range covered in these experiments, but are probably small for Cr-Al thermocouples.[10,11]

One serious problem was encountered during data reduction. Lee and Mardon[12], among others, have reported that the α-β and β-γ transitions are very sensitive to heating rates while the others are less affected. Our

results also show this. The data for the α-β and β-γ transitions did not extrapolate to the correct temperatures at 1 atmosphere, while the other transitions did. This phenomenon was due, at least in part, to the very rapid heating rates used. The rapid rates, about 7 °C/sec, were necessary to obtain sharp DT signals.

During all runs an attempt was made to keep the heating rate constant for all transitions and to keep it as low as possible. No data were plotted for extremely fast heating rates. However, sufficient data were obtained on the effect of heating rate on the transitions at various pressures so that proper corrections could be made. These data, although rough, showed that the sensitivity of transition temperatures of the α-β and β-γ transitions decreases approximately linearly from its maximum effect at 1 atmosphere to zero at 20 kilobars. Above 20 kilobars the transitions seemed unaffected by heating rate. This result was used to correct the temperatures in the following manner. The temperature correction to force the experimental data to fit the correct 1-atmosphere values was decreased linearly from its maximum value at 1 atmosphere to zero at 20 kilobars. The errors introduced by this method are discussed later.

Samples

Plutonium samples of 99.85% purity, obtained from Dow Chemical Company at Rocky Flats, Colorado, and of 99.9% purity, obtained from Los Alamos Scientific Laboratory, were used in this work. Data obtained with both types agreed within experimental error.

RESULTS AND DISCUSSION

The experimentally derived phase diagram for plutonium is shown in Fig. 3. The results shown represent the data from seven DTA runs and two volume discontinuity runs. Data of Bridgman[5] and McWhan et al.[6] are included for comparison. Our methods were not sensitive enough to detect the δ-δ' transition. No new phases were observed. The triple point data and initial slopes of the transitions are shown in Table 2, where some predicted values of Loasby[13] are also shown for comparison.

Table 2. Triple points and initial transition slopes

Triple point	Experimental values	Predicted by Loasby[13]
γ-δ-ϵ	398 ± 10°C	374°C
	0.9 ± 0.2 kilobar	0.69 kilobar
γ-ϵ-liquid	518 ± 10°C	
	19.5 ± 1 kilobar	
β-γ-liquid	500 ± 10°C	
	27.0 ± 1 kilobar	

	Initial slope of transition lines, °C/kbar	
Transition	Experimental slope	Predicted by Loasby[13]
α-β	11.2	13.1
β-γ	27.3	38
γ-δ	88	95
δ-ϵ	-87	~-190
ϵ-liquid	-4.4	-26

The higher pressure data are believed to be accurate to ±1 kilobar and the lower pressure data to ±0.2 kilobar. The pressures could be read to ±0.5% and the reproducibility of the higher pressure data was within ±0.5

kilobar. However, due to the uncertainties of the actual degree of hydrostaticity of the talc and sample assembly, an error of ±1 kilobar seemed more realistic.

The temperatures were reproducible to ±10°C. There seemed to be no corrosion or alloying of the Pu on the Ta capsule. The temperatures are believed accurate to ±10°C with the exception of the β-γ transition, which is believed accurate to ±20°C. The maximum temperature mentioned previously to correct the α-β transition data was 21°C, but the maximum correction for the β-γ transition was 53°C. If the correction taken was not truly linear, this could introduce a much larger error in the β-γ transition than indicated, hence an error of ±20°C is assigned.

Loasby[13] has predicted the initial slopes of the transitions and the location of several triple points. It may be seen that the predicted γ-δ-ε triple point agrees with the experimental values almost within experimental error. However, above 1 kilobar the predictions break down, as β-γ-ε and β-ε-liquid triple points are predicted which did not occur experimentally. This is probably due to the assumption of the $\Delta V/\Delta H$ in the Clapeyron equation remaining constant to high pressures.

Data of previous investigators on the α-β transition seem to agree with the present work within the combined experimental error. Bridgman's[5] data at 3100 and 7060 kg/cm^2 lie about 10°C above the equilibrium line in Fig. 3. The data of McWhan et al.[6] agree well with the present work to 10 kb but are about 14°C lower at 17.5 kilobars.

The slope of the melting curve is negative until the β-γ-liquid triple point is obtained. From this point on the slope is positive. This is in qualitative agreement with the behavior of many other metals with a negative initial melting curve. Eventually a solid-solid-liquid triple point is met, after

which the melting slope becomes positive. Examples of this include Bi[14-16], Ga[14,17], Sb[8], and InSb.[18]

Some metastability of the α-β transition was noted, in agreement with the reports of many workers. The metastability seemed to decrease sharply with increasing pressure, however, as no such signals were detected over 10 kilobars.

Acknowledgement—I wish to express sincere appreciation to Mr. Eben Lilley who assisted in the design and execution of this experiment and participated in all data runs. I would also like to thank Dr. William Ramsey for allowing us to use many experimental facilities and for critically reviewing the manuscript. The work was done under auspices of the U. S. Atomic Energy Commission.

REFERENCES

1. Wilkinson W. D. (Ed.), Plutonium and Its Alloys. Interscience Publ., New York (1960).
2. Grison E., Lord W. B. H. and Fowler R. D. (Eds.), Plutonium 1960. Cleaver-Hume Press, London (1961).
3. Coffinberry A. S. and Miner W. H. (Eds.), The Metal Plutonium. University of Chicago Press, Chicago (1961).
4. Zachariasen W. H., in reference 3. p. 99.
5. Bridgman P. W., J. Appl. Phys. 30, 214 (1959).
6. McWhan D., Montgomery P. W., Stromberg H. D. and Jura G., J. Phys. Chem. (to be published).
7. Boyd F. R. and England J. L., J. Geophys. Res. 65, 741 (1960).
8. Kennedy G. C. and Newton R. C., in Solids Under Pressure. McGraw-Hill (to be published).
9. Bridgman P. W., Proc. Am. Acad. Arts & Sci. 74, 21 (1940).
10. Birch F., Rev. Sci. Instr. 10, 137 (1939).
11. Bundy F. P., in Progress in Very High Pressure Research, p. 256. John Wiley & Sons, New York (1960).
12. Lee J. A. and Mardon P. G., in reference 3, p. 133.
13. Loasby R. G., in reference 2, p. 97.
14. Bridgman P. W., Phys. Rev. 48, 893 (1935).
15. Butuzov V. P., Soviet Phys.-Cryst. (English Transl.) 2, 533 (1957).
16. Bundy F. P., Phys Rev. 110, 314 (1958).
17. Jayaraman A., Klement W. Jr., Newton R. C. and Kennedy G. C., J. Phys. Chem. Solids (to be published).
18. Jayaraman A., Newton R. C. and Kennedy G. C., Nature 191, 1288 (1961).

/sh

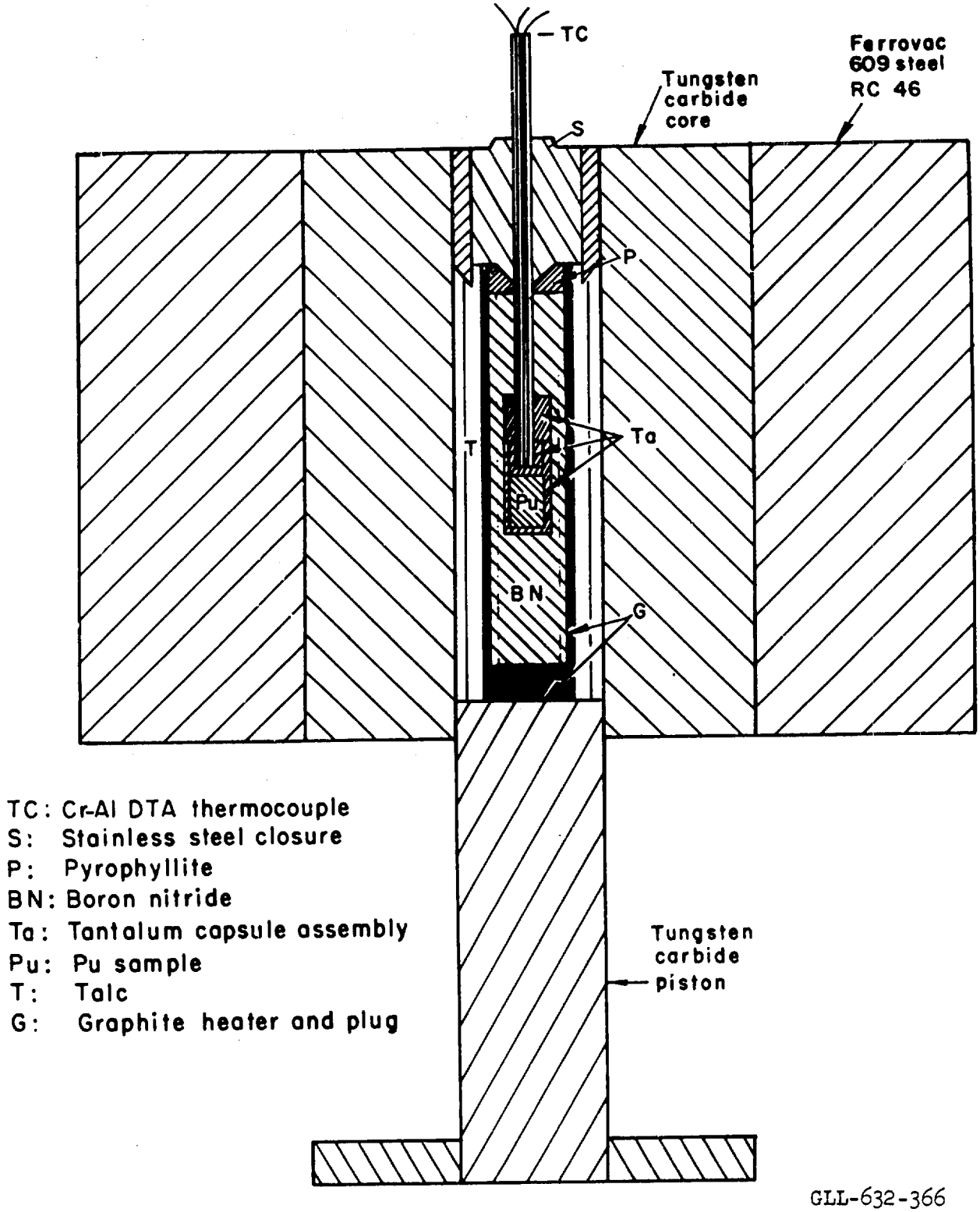
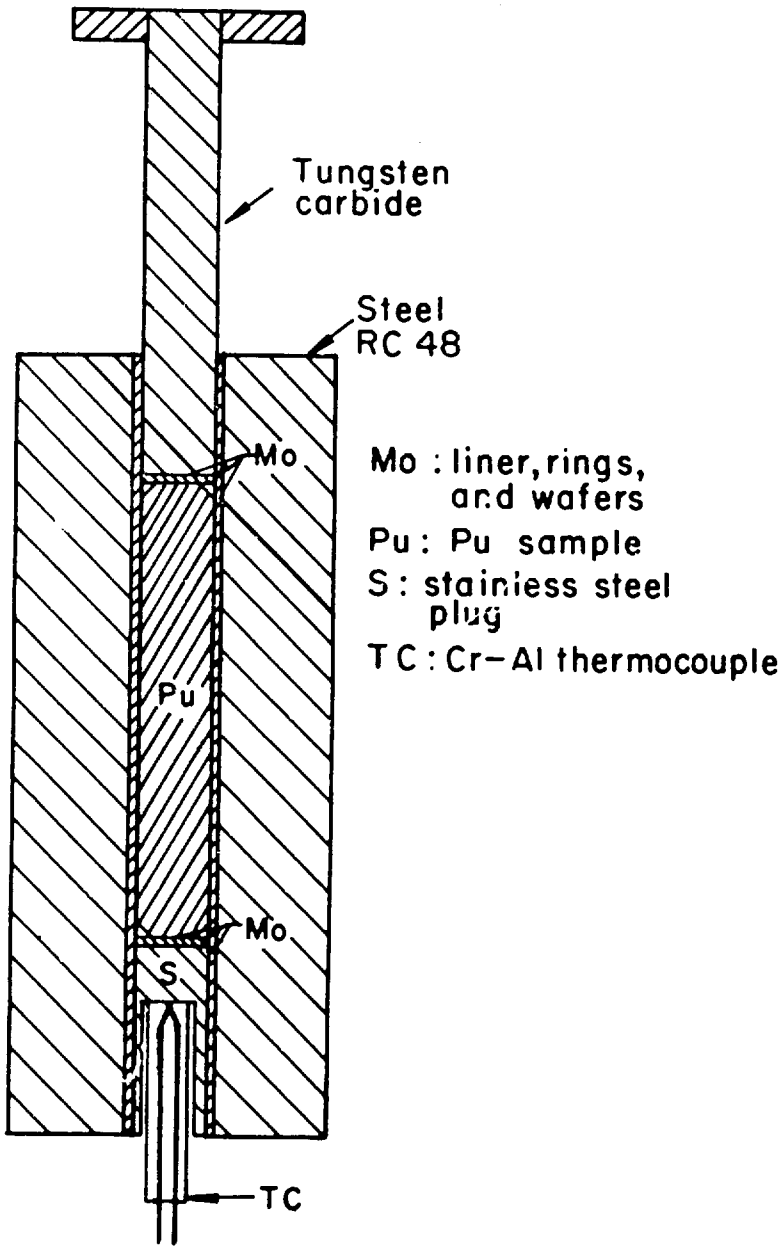


Fig. 1. High pressure apparatus for differential thermal analysis (DTA).



GLL-632-367

Fig. 2. High pressure apparatus for volume discontinuity.

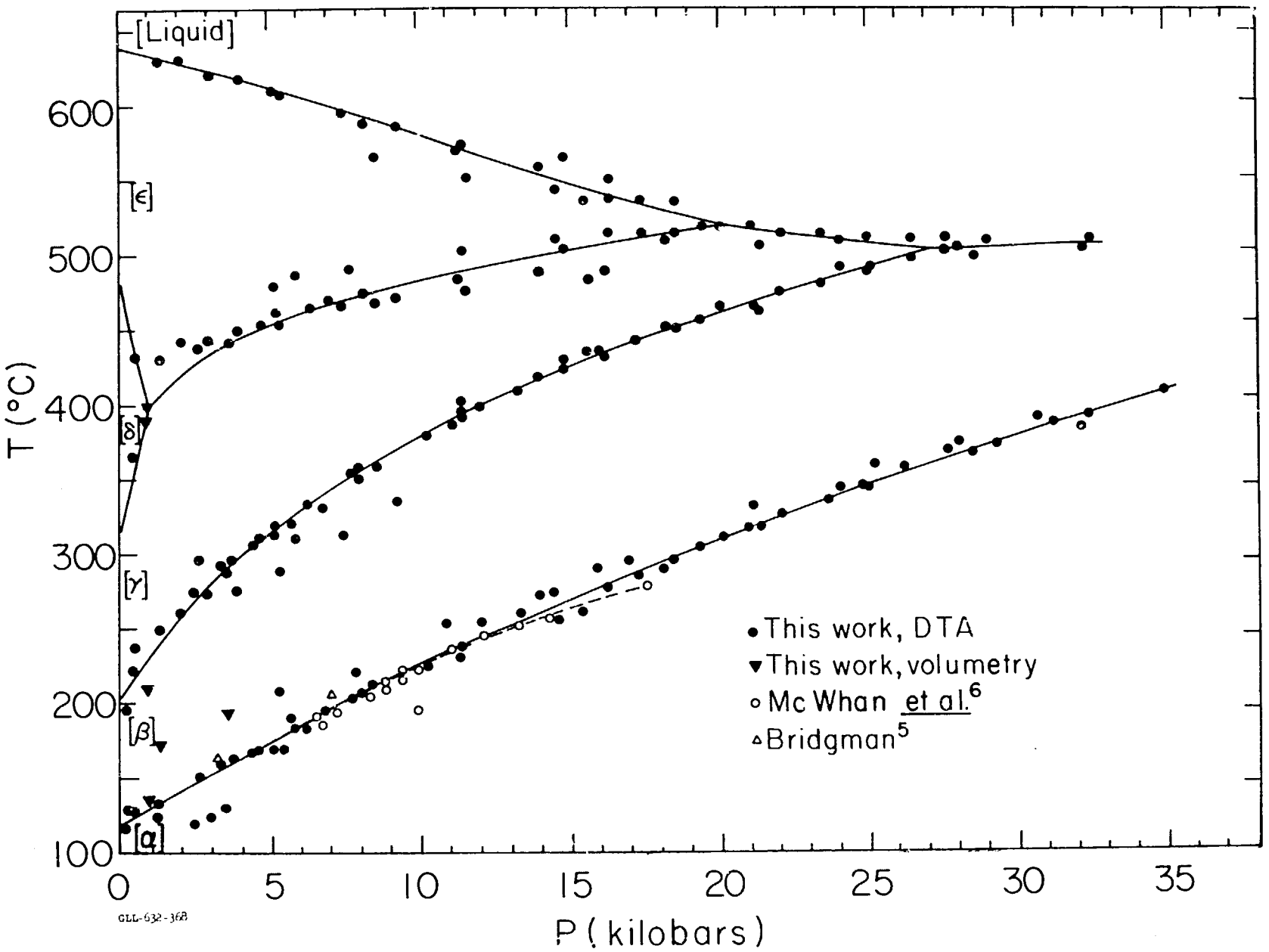


Fig. 3. The phase diagram of plutonium.