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Reprinted from JOURNAL OF APPLIED PHYSICS, Vol. 30, No. 2, 214–217, February, 1959

Printed in U. S. A.

Compression and the α-β Phase Transition of Plutonium

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(Received July 30, 1958)

Recent lifting of the security restrictions now permits publication of measurements of various effects of pressure on plutonium made during the war. Compressions on the alpha phase were measured at room temperature to 40 000 kg/cm² in one apparatus and to 100 000 in another. The total volume compression under 100 000 is very close to 10%. Compressibility decreases with increasing pressure as is normal. Exploration for other transitions was made to 20 000 kg/cm² at 100° and 200°—none were found. The pressure and the volume change of the alpha-beta transition was measured at 162.6° and 205°. The transition curve is "normal," the pressure rising with increasing temperature with downward curvature, and volume increment decreasing. The volume increment averages nearly 9%. The pressure of transition at 205° is very approximately 7000 kg/cm². The calculated latent heat of transition at the mean pressure is roughly 4.5 cal/g.

INTRODUCTION

THIS paper reports the results of various measurements of the effect of static hydrostatic pressures on plutonium made during the spring of 1945. The security restrictions have just been lifted, permitting publication in full detail now for the first time, although a partial publication in summary has been previously published. I am indebted to Dr. Henry L. Laquer of the Los Alamos laboratory for his active interest in this matter and for acquainting me with all the declassified work on plutonium published up to November, 1957.[1]

The measurements comprise: (a) volume measurements at room temperature with two different types of apparatus, the first with rather good accuracy to 40 000 kg/cm², and the second with much inferior accuracy to 100 00 kg/cm²; and (b) measurements of the effect of pressure up to a temperature of 205°C of the phase change which normally occurs at atmospheric pressure in the neighborhood of 115°C.

The measurements were made in the Lyman Laboratory of Harvard University with apparatus and by methods already developed and described in detail,[2] except for unessential modifications to guard against probable effects of possible accidental explosions. The various piezometers were set up with their charges of plutonium at Los Alamos and transported to Cambridge by special messenger, who returned the material to Los Alamos after the measurements had been completed. At Los Alamos, Dr. Cyril S. Smith and Dr. Eric R. Jette were in immediate charge of the arrangements. The material was the best available at the time, with an impurity content of the general order of 0.1 wt %. It was not in a perfectly well defined condition, as shown by variations of the initial density between the different samples. The total quantities of plutonium were approximately 3.5 g for the transition studies, 1.5 g for the compressibility measurements to 40 000, and 0.1 g for the compression measurements to 100 000. The actual measurements for the transition studies were made by Mr. L. H. Abbot; the other measurements and all the computations were made by me.

DETAILED DATA

Compressions to 40 000

Two different pressure containers were used, giving measurements on two different specimens of plutonium. It was intended to make two complete sets of independent measurements with each pressure container, but various mishaps (breakage of a piston and inadvertent contamination during one filling) reduced the number of good measurements to one run to 40 000 with one container, and two independent runs to 25 000 and 40 000, respectively, with the other.

In these measurements to 40 000 the container is subjected to both external and internal pressure, thus minimizing the elastic expansion of the bore. The pressure is transmitted by indium. Because of the approximate equality of diameter and length of the charge, frictional and other hysteretic difference between measurements with increasing and decreasing pressure is less than 5% of the maximum effect. The total corrections for compression of the indium transmitting medium and distortion of the apparatus are of the order of only 40% of the total measured effect. All these factors are unusually favorable for measurements of compression. The deviation of any single reading from a smooth curve was seldom as much as 1% of the total pressure effect.

In Table I are shown the relative volumes to 40 000 kg/cm² as given by measurements with the two containers. The initial density of the material in container III, as determined at Los Alamos with a slight correction for initial compaction, was 19.47, and that in container II 19.66. If the readings with container

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[1] A. S. Coffinberry and M. B. Waldron, Progr. in Nuclear Energy, Ser. V **1**, 354–410 (1956). This paper contains references to all the published work up to time of publication. There is a later paper: M. B. Waldron, Atomics, 383–386 (October, 1957).

[2] P. W. Bridgman, Proc. Am. Acad. **76**, 71–87 (1948), for compressions to 40 000; **76**, 55–70 (1948) for compressions to 100 000 **74**, 399–424 (1942) for transitions to 50 000.

III are taken at their face value a reversible transition in the neighborhood of 900 kg/cm^2 with fractional volume change of 0.0047 is indicated. However, no trace of such a transition was found with the other container, nor was it found during a repetition of the measurements with number III. The other measurements on this repetition were vitiated as far as calculations of exact compressions is concerned because of splitting of the carboloy piston, but they should be competent to indicate the presence or absence of the transition. This possible transition was therefore ignored in the calculations summarized in the table. A possible explanation of the apparent transition is a reversible buckling of a flat steel washer at the lowest pressure of the range, but there was no opportunity to check this.

The measurements to 25 000 maximum with container II afford a valuable check on the reliability of the deviations from linearity of the change of volume with pressure. Other things being equal, the accuracy of a deviation from linearity increases with the square of the pressure range, and hence should be 2.5-fold greater for the 40 000 range than for the 25 000 range. The deviation from linearity of the proportional volume decrement at the midpressure, 12 500, of the measurements to 25 000 was 0.0021, and the corresponding figure at the same pressure from the measurements over the 40 000 range was 0.0023. This agreement is as good as one has a right to expect, and should give confidence in extrapolating the volumes to considerably higher pressures.

Only the measurements from the two 40 000 ranges have been incorporated into the table. The compressibilities to be deduced from the volumes in Table I agree reasonably well with determinations of compressibility made by Laquer by a pulse technique up to 2000 kg/cm^2 as reported by Coffinberry and Waldron.

Compressions to 100 000

The material is confined in a carboloy piezometer jacketted with steel, which is enclosed in a second pressure vessel and exposed, for support, to a uniform hydrostatic pressure of between 25 000 and 30 000 kg/cm^2 over the entire external surface. The material is compressed by two pistons, driven into the piezometer from the two ends. The force driving the pistons is measured with an independent device also exposed to the supporting pressure. The speciman is enclosed in an indium sheath to transmit pressure approximately hydrostatically, but because the diameter is of the order of only one-quarter of the length, the frictional and hysteretic effects are much greater than with the 40 000 apparatus. This apparatus gives its best results only for materials of relatively high compressibility—plutonium is not one of them.

TABLE I. Volume compressions to 40 000.

Pressure kg/cm^2	V/V_0 Container II	Container III	Average
0	1.0000	1.0000	1.0000
5000	0.9907	0.9909	0.9908
10 000	0.9822	0.9828	0.9825
15 000	0.9745	0.9756	0.9750
20 000	0.9675	0.9690	0.9682
25 000	0.9612	0.9629	0.9620
30 000	0.9555	0.9571	0.9563
35 000	0.9503	0.9514	0.9508
40 000	0.9455	0.9460	0.9457

TABLE II. Volume compressions to 100 000.

Pressure kg/cm^2	V/V_0 Average II and III	Average 3 piezometers
0	1.0000	
5000	0.9908	
10 000	0.9825	
15 000	0.9750	
20 000	0.9682	
25 000	0.9620	0.9620
30 000	0.9563	0.9561
35 000	0.9508	0.9504
40 000	0.9457	0.9448
50 000		0.9335
60 000		0.9242
70 000		0.9161
80 000		0.9092
90 000		0.9032
100 000		0.8981

Measurements were made with three different piezometers to maximum pressures, respectively, of 97 700, 92 300, and 100 900 kg/cm^2. Five piezometers had been planned for, but there were mishaps with two. The density of this material was not determined at Los Alamos. Determinations by me, of quite inferior accuracy, from the dimensions and with subtractive corrections of over 50% for the value occupied by the indium etc. gave for the respective initial densities 21.1, 19.5, and 20.0; the apparent variation is doubtless not real.

The chief value of these measurements to 100 000 is in indicating whether there are any new important transitions. All three runs showed irregularities which are not inconsistent with a small reversible transition. If the transition is real it runs with increasing pressure between 73 000 and 84 000, between 57 000 and 68 000, and between 48 000 and 55 000 for the three fillings, respectively, and with decreasing pressure between 47 000 and 41 000, between 61 000 and 51 000, and between 38 000 and 31 000, respectively. The great variation in these figures could be explained by stickiness of the transition and by overshooting. The figures are not inconsistent with the existence of a transition thermodynamically reversible somewhere between 51 000 and 55 000. The volume change of such a transition could not be more than 1%. However, it seems to me that the balance of probability is against it, and in the following I have smoothed the volume decrements right over any such possible transition.

The relative volume as a function of pressure, averaged for the three piezoemeters, is shown in Table II. The zero for these computations is the volume at 25 000 given by the other apparatus. The results for the individual piezometers varied considerably, from 0.0090 to 0.0106 for the total fractional volume decrement between 25 000 and 100 000. The two first fillings gave results within 2% of each other and 15% less than the third filling. The arithmetical average, therefore, as given in the table, probably errs in giving volume decrements which are too large.

Taken at their face value, the figures of Table II indicate a drop of compressibility at 100 000 to between 0.25 and 0.30 of its initial value at atmospheric pressure.

Plutonium thus appears as a substance of median over-all compressibility. Its volume at 100 000 of 0.898, may be compared with volumes of 0.884, 0.910, and 0.915 for arsenic, zirconium, and aluminum, respectively. The original exceptation was that the compression of plutonium would prove to be materially higher.

Effect of Pressure on the α-β Transition

Measurements were made with a single filling of a single container in my regular apparatus for the study of compressions and transitions up to 50 000 kg/cm^2 and up to 250°. The plutonium was encased in a lead capsule, instead of indium as in the compression measurements. Before starting these measurements it was known that there is a transition at atmospheric pressure at approximately 117°, the density being said to drop with rising temperature from 19.8 to 17.5, that is, with a volume decrement of 13%. It was therefore to be expected that the transition would run at higher temperatures with increasing pressure, but without knowledge of the heat of transition the expected rate of rise with pressure was not calculable.

The present measurements consisted in the first place of exploratory applications of pressure to 20 000 kg/cm^2 at 100° and 200°. This exploration was sensitive enough to detect volume changes of 0.0002 of the initial volume. It was thus established that there was no new transition under these conditions between atmospheric pressure and 20 000 at 100°, and at 200° no transition except the expected one at comparatively low pressure.

The transition parameters were determined at 205°, 163°, and again independently at 205° by the method of piston displacement at constant temperature, and at about 1600 kg/cm^2 by the method of lowering temperature at constant piston displacement. The latter was by way of check, the transition running catastrophically and irreversibly in the region of thermodynamic instability. The first method, however, gives the reversible parameters. Here the general idea is to so manipulate the pressure as to force the material to be approximately equally divided between the two phases. Small pressure displacements are then made in either direction until the transition can just be observed to be running in one direction or the other. The mean is taken as the pressure of thermodynamic equilibrium. After equilibrium pressure is thus determined pressure is pushed far enough beyond the equilibrium pressure to force the transition to run to presumptive completion in either direction, thus permitting a determination of the total volume change of the transition.

The temperatures given in the following are the temperatures of the thermostatically controlled temperature bath. No correction was attempted for any self-heating due to radioactivity; under the conditions any such effect should be small. The same remarks apply to the measurements of compressibility. The results are shown in Table III.

In general, this transition ranks high among the clean-cut transitions. It starts without much over shooting in either direction, apparently runs to completion within a moderate pressure range, and the equilibrium pressure can be enclosed within tolerably narrow limits.

On the check run with decreasing temperature at constant volume, at a rate of approximately 0.5° per min, the transition ran catastrophically, apparently to completion, somewhere between 100° and 75°. The equilibrium temperature was thus over passed by somewhere between 40° and 65°. The indicated fractional change of volume under these conditions was 0.0818, much lower than the change to be expected according to the data of Table III at this pressure under equilibrium conditions. The value 0.0818 would suggest that the thermal expansion of the high-temperature phase is materially higher than that of the low-temperature phase, a result which does not agree with the general consensus of other observers as reported by Coffinberry and Waldron. The discrepancy can be explained by a small undetected running of the transition before the catastrophic drop, or incomplete running of the transition.

Any reasonable extrapolation to atmospheric pressure of the volume changes measured under pressure would indicate a probable value distinctly less than the originally expected 13% already mentioned, and within the range 8.30 to 11.03% permitted by the values quoted by Coffinberry and Waldron.

Comparison of the slopes of the isotherms above and below the transition indicates that the compressibility of the alpha phase is about 20% less than that of the

TABLE III. Effect of pressure on the $\alpha-\beta$ transition.

	Pressure of beginning of transition, kg/cm^2			Volume change on transition fractional, $\Delta V/V_0$ cm^3/g		
Temperature	from above	from below	mean	decreasing pressure	increasing pressure	mean
205.1°C	8250	5880	7060	0.0879	0.0951	0.00437
162.6	4650	1550	3100		0.0893	0.00452
204.9	8250	5880	7060	0.0870		0.00439

beta phase. A difference in this direction would be expected because of the large difference in density.

Linear extrapolation to atmospheric pressure of the equilibrium pressures and temperatures indicated in Table III gives a transition temperature of 129.4°. This is distinctly higher than any of the transition temperatures indicated in the literature, showing that in all probability the transition line is concave toward the pressure axis, which is the normal direction of curvature.

The transition data permit a calculation of the heat of the transition, a quantity apparently not yet determined by direct experiment. The data of Table III give at the mean equilibrium pressure and temperature of 5080 kg/cm^2 and 183.8°C a latent heat of transition of 190 kg cm/g (approximately 4.45 cal/g), and by a rough extrapolation 130 kg cm/g at atmospheric pressure, assuming a transition temperature of 120.0°.

Qualitatively the transition appears normal in the most important respects—transition temperature rising with increasing pressure with downward curvature, and a volume change decreasing with increasing temperature and pressure. Quantitatively, the volume change is high.