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THE THERMAL EXPANSION OF PLUTONIUM METAL BELOW 300°K

by

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ABSTRACT

Curves for linear expansion of plutonium metal as a function of temperature below 300°K are shown for different cooling and heating cycles and for different purity. Hysteresis and time effects were found to be appreciable. The linear expansion curve obtained with very slow cooling or very slow warming rates appears to confirm the presence of two of the three major heat capacity peaks found in the temperature range below 160°K. Evidence for existence of an antiferromagnetic state in plutonium seems to be provided.

A curve for the linear expansion of oxygen-free, high conductivity copper below 300°K is also given.

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1. INTRODUCTION

Originally, the existence of three major heat capacity peaks for plutonium metal between 4°K and 300°K, as first reported by Sandenaw, Olsen, and Gibney,[1] was questioned. There were no published data on the crystal structure of plutonium at low temperatures, and measurements of thermal expansion between 80°K and 298°K [2, 3] had shown nothing unusual. There was, then, no evidence of any kind to suggest that heat capacity anomalies should be expected at low temperatures.

The thermal expansion study reported here was undertaken in spite of other negative data because it seemed to be the surest and simplest way of looking for unknown phases or metastable states in the temperature region below 300°K. It was known that processing played an important role in appearance of low temperature heat capacity peaks and that thermal expansion was a property that could be measured during temperature cycling at almost any desired rate.

2. SPECIMEN DESCRIPTION

One of the specimens chosen for thermal expansion measurements was not of sufficient quality to be called high purity, but analysis showed it to contain 99.9% plutonium. A reason for its choice was that

the combined iron and nickel content was only 150 ppm. Although this was not comparable to high purity plutonium, it was nevertheless good. Another reason for choosing it was the high degree of reproducibility found in electrical resistivity measurements made on this same specimen down to 1.73°K (specimen No. 1 of electrical resistivity measurements reported by Sandenaw and Olsen.[4]) Specimen dimensions (after remachining) were: length, 1.503 in. and diameter, 0.172 in. Density was 19.55 g/cm^3.

The second plutonium specimen chosen for examination in the thermal expansion apparatus was one that had been cast with added iron to give a final iron content of 600 ppm. The remaining elements, reported as impurities in this second test specimen, were present in even lower quantities for some elements than in specimen No. 1. Dimensions of the second specimen were as near to those of the first specimen as machining allowed, and density was 19.20 g/cm^3.

Preliminary checks of the thermal expansion apparatus were made using annealed, oxygen-free, high conductivity (OFHC) copper and clear, fused quartz. These specimens were fabricated to as near the above dimensions as was practical.

3. EXPERIMENTAL DETAILS

3.1 Apparatus

The thermal expansion apparatus was built around a Schaevitz Engineering Type 100 M-L linear variable differential transformer which

required an excitation frequency of 10,000 cps at 3 volts. The linear range of this transformer was ± 0.1 in.

The specimen holder was kept to a minimum size so that all parts of the transformer and test specimen could be completely immersed in liquid helium or other liquefied gas during cooling or processing. The schematic structure of the specimen holder and linear variable differential transformer is shown in Fig. 1. Size of the over-all assembly can be judged from the specimen length of 1.5 in.

The body of the specimen holder was made of copper because of its good low temperature thermal conductivity. It was machined in sections for ease of insertion of the linear differential transformer and replacement of test specimens. To prevent shifting of the transformer, it was spring loaded against its seat in one section of the body. The copper pusher, which was tightly screwed into the threaded section of the transformer core, was lightly spring loaded against the test specimen of OFHC copper, quartz or plutonium. The slotted screw in the lower part of the assembly was for adjusting the transformer core to the center of its linear range.

The upper portion of the holder was tightly packed with glass wool, which was inserted carefully around the transformer leads. This was done because the specimen holder was evacuated through holes drilled in the upper Inconel connector. The glass wool filtered out all oxides of plutonium formed during treatment and processing and kept the inside of

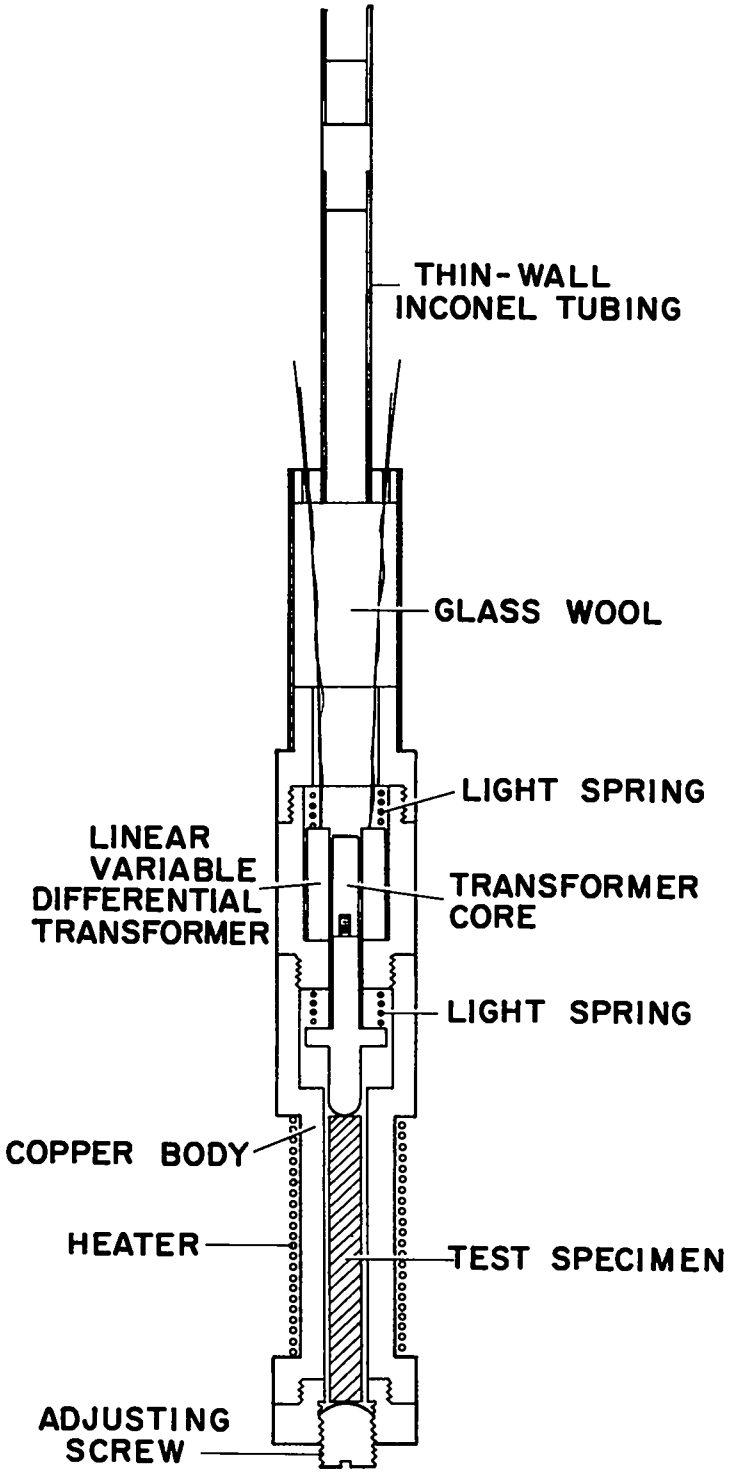

Fig. 1. Thermal expansion apparatus

the double dewar vacuum system from becoming contaminated.

A resistance heater was wrapped around the lower section of the assembly so that, with radiation losses to the liquid nitrogen in the outer dewar, the temperature of the assembly could be maintained within a narrow range for long periods.

Temperature was measured with thermocouples of gold-2.11 atomic percent cobalt vs copper. These were fastened to the copper body just above the resistance heater. The output of one thermocouple was fed to the y-coordinate of a Brown x-y Recorder. The other thermocouple leads went to a Brown Recorder which had a range of 40 mv in 40 steps of 1 mv each. (This recorder and calibration of thermocouples have been described in a report on the heat capacity of copper.[5])

The output of the linear variable differential transformer was rectified and part of the rectified voltage was bucked out by a standard mercury cell and helipot circuit. The remaining signal was fed to the x-coordinate of the Brown x-y Recorder as a record of specimen length. At maximum sensitivity in the linear range of the differential transformer, a motion of 5×10^{-3} in. was equivalent to 8.15 cm on the chart paper. This sensitivity was maintained for at least 0.030 in. of the 0.100 in. linear range on each side of the null or balance point. Maximum change of length of any specimen was less than 0.014 in.

3.2 Experimental Procedure

It is evident from the construction of the assembly that the

thermal expansion measured must be relative to that of some other material whose expansion properties are known and consistent. The standard chosen was clear, fused quartz.[6] It is also apparent that, since the linear variable differential transformer was itself to be cooled by liquid helium and maintained at all times at specimen temperature, its output at a given temperature would vary as compared to its room temperature output. However, it was felt that if temperature equilibrium were maintained, the transformer output should not vary from run to run or from specimen to specimen. The constancy of this standard had to be assumed, but confidence in it is given by the results for copper described below.

In order to calibrate the differential transformer, an OFHC copper specimen was placed in the apparatus with the lowest copper section of the specimen holder removed. The specimen extended approximately 0.25 in. beyond the remaining copper body. A micrometer which could be read 1/10,000 in. (and estimated to 1/100,000 in.) was fastened to the copper body by an adapter. Motion at the end of the specimen relative to this body was measured accurately by the micrometer and related to motion of the pen on the chart, representing transformer output. Bucking voltage (i.e., dial settings) and chart reading were determined as functions of change in specimen length for the entire linear range of the transformer.

After removal of the micrometer, the end section of the copper body was replaced. The bottom screw was adjusted to get the transformer

core to the position of maximum circuit sensitivity, and all screw connections in the copper body were tightly taped with adhesive-backed glass tape to prevent accidental unscrewing during the experiment. The OFHC copper specimen was then studied in the temperature range ~2.0°K to room temperature.

An accurately measured fused quartz specimen of the same length was then placed in the holder. A complete study of transformer core motion, sensitivity, and other properties was made with the quartz specimen to insure that the Hewlett Packard Audio Oscillator (Model 200C), the rectifier circuit, linear variable differential transformer, x-y recorder, etc., gave reproducible results on removal of one type of specimen and replacement with another. Since reproducibility was found to be excellent, the quartz specimen was then studied between ~2°K and 300°K.

Plutonium was known to show hysteresis effects, so it was checked for thermal expansion during three different cycles of cooling and heating. These were:

1. The specimen was cooled from room temperature to ~2°K, then warmed back toward room temperature in one 8 hour day.
2. The specimen was cooled rather rapidly to 76°K and then cycled between 76°K and 48°K for 2 days. From 76°K, the specimen was cooled to 3.96°K. It was held at 3.96°K and below for 75 minutes. Next the specimen was warmed slowly to above 70°K, and then

allowed to cool back to 52°K. Finally it was warmed from 52°K to 300°K in 3-2/3 hours.

3. The specimen was cooled from room temperature to ~48°K very slowly, over a 27-1/2 hour period. The reverse warming cycle was then done even more slowly, over a period of 6 days.

4. EXPERIMENTAL RESULTS

4.1 OFHC Copper

The curve for thermal expansion of the OFHC copper specimen relative to fused quartz is shown in Fig. 2. The extremes in the scatter of the points are shown in this figure. The results compare quite well with data of Rubin, Altman, and Johnston[7] for the temperature range 40°K to 200°K. The linear contraction between 273.15°K and 2°K (Fig. 2) is about 3% greater than that of Rubin et al.[7]

4.2 Normal-Purity Plutonium

Two curves for the thermal expansion of normal-purity plutonium metal relative to fused quartz are shown in Fig. 3. The curve for rapid cooling and warming of the plutonium specimen is shown as the dashed line. The values for cooling and warming coincided within experimental error above 76°K and the curve was smooth.

The curve for the slowest cooling of normal-purity plutonium is shown as the solid line in Fig. 3, and is very different from the other curve shown on this figure. The specimen had a high coefficient

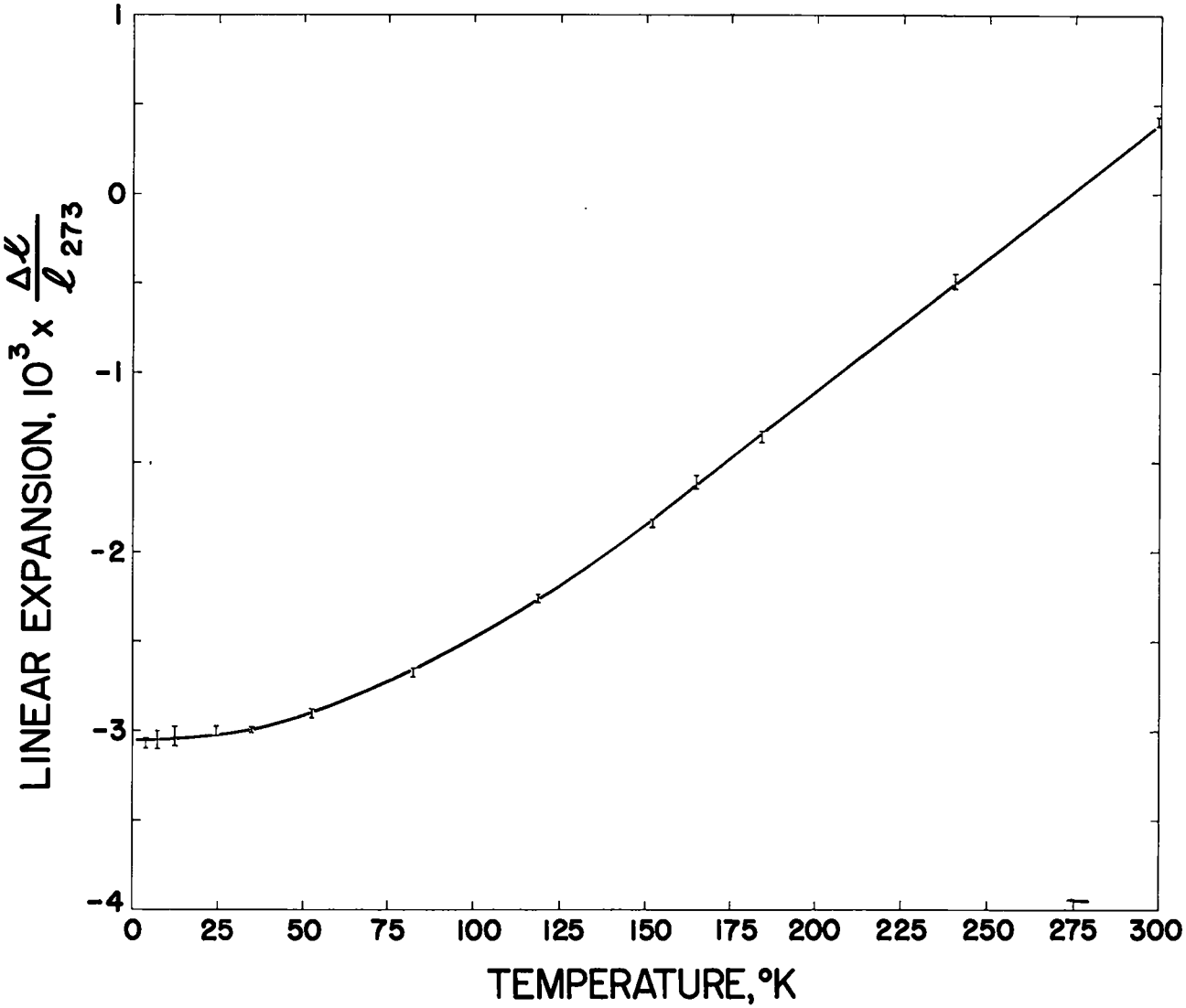

Fig. 2. Thermal expansion of OFHC copper below 300°K (relative to fused quartz)

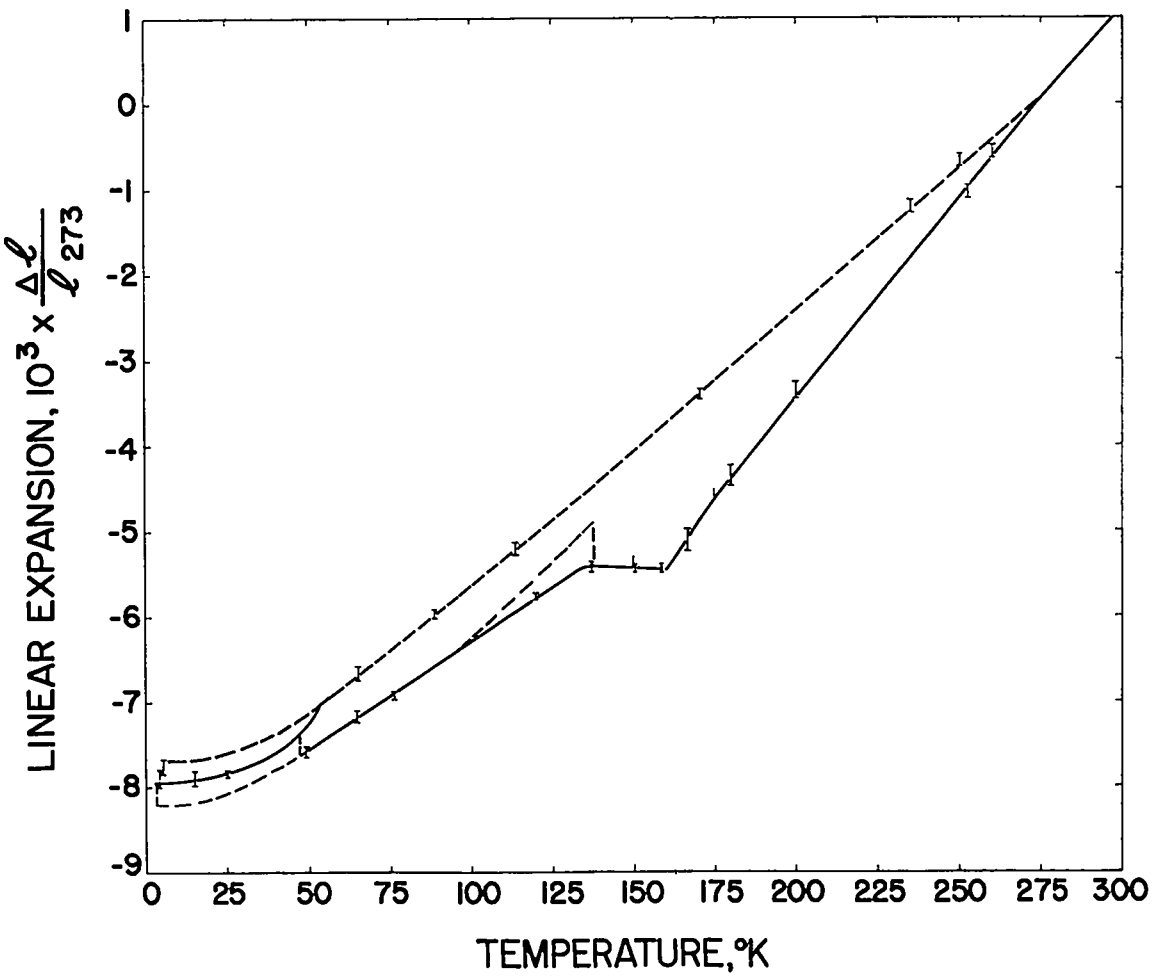

Fig. 3. Thermal expansion of normal purity plutonium metal relative to fused quartz: a) Top dashed line represents curve for relatively rapid cooling and warming; b) Solid line between ~48°K and 300°K represents results found in 27-1/2 hour cooling period; c) Solid line between 2°K and 60°K represents results from warming trend.

of thermal expansion down to ~160°K, then zero contraction on further cooling to ~135°K. The contraction was linear from 135°K to ~48°K, and on holding for one hour at this latter temperature, an expansion was observed. The solid line, as shown between 4°K and 60°K, represents thermal expansion during a slow warming trend. On holding for one hour and letting the temperature drop back to 52°K, a contraction to the previously observed value for this temperature resulted. The reversible offset is represented by the vertical dashed line. At the extremely slow warming rate used, the expansion curve followed the cooling curve from 52°K up to 95°K where it diverged. Between 95°K and 140°K the curve representing very slow warming could not be made to follow that of very slow cooling. At 140°K, however, the experimental points dropped back on the "slow" cooling curve; and above this temperature the curves for slow warming and slow cooling were identical within experimental error. The final stopping point on the chart was within 0.3% of the initial starting point of one week earlier.

It should be pointed out that the thermal expansion phenomenon observed below 52°K in Fig. 3 represented a hysteresis loop. In a liquid helium run, the specimen was cooled from 76°K to 3.96°K in a 30 minute period. Readings were taken, and a slight continuous contraction was noticed. The specimen started to expand within a few minutes after reaching 3.96°K, and this expansion continued until apparent equilibrium and stability was reached nearly an hour later.

On warming, the contraction was observed at a temperature of ~50°K (as noted above).

4.3 Plutonium with 600 ppm Iron Content

The curve for the thermal expansion of plutonium metal having an iron content of 600 ppm is shown as the solid line in Fig. 4. The similar curve for normal purity plutonium is shown as a dashed line on this figure for comparison.

The expansion curve for the metal with the high iron content was not truly similar to the other curve over any temperature range. The offset at ~50°K was not observed with the high iron specimen, and the scatter of values obtained on warming or cooling was generally much greater than with the first specimen. Also, longer times were required to get equilibrium values with this specimen.

4.4 Least Squares Equation for Linear Expansion of OFHC Copper Below 273°K

The thermal expansion data for OFHC copper has been submitted for least squares analysis utilizing the IBM 704 Computer. The equation for the linear expansion of OFHC copper as a function of temperature below 273°K was determined to be as follows:

Temperature Range: 2°K to 273°K

$$\Delta l_T = l_{273} (A + BT + CT^2 + DT^3)$$

where

$$A = -3.0360448 \times 10^{-3}$$

$$B = -8.8783809 \times 10^{-7}$$

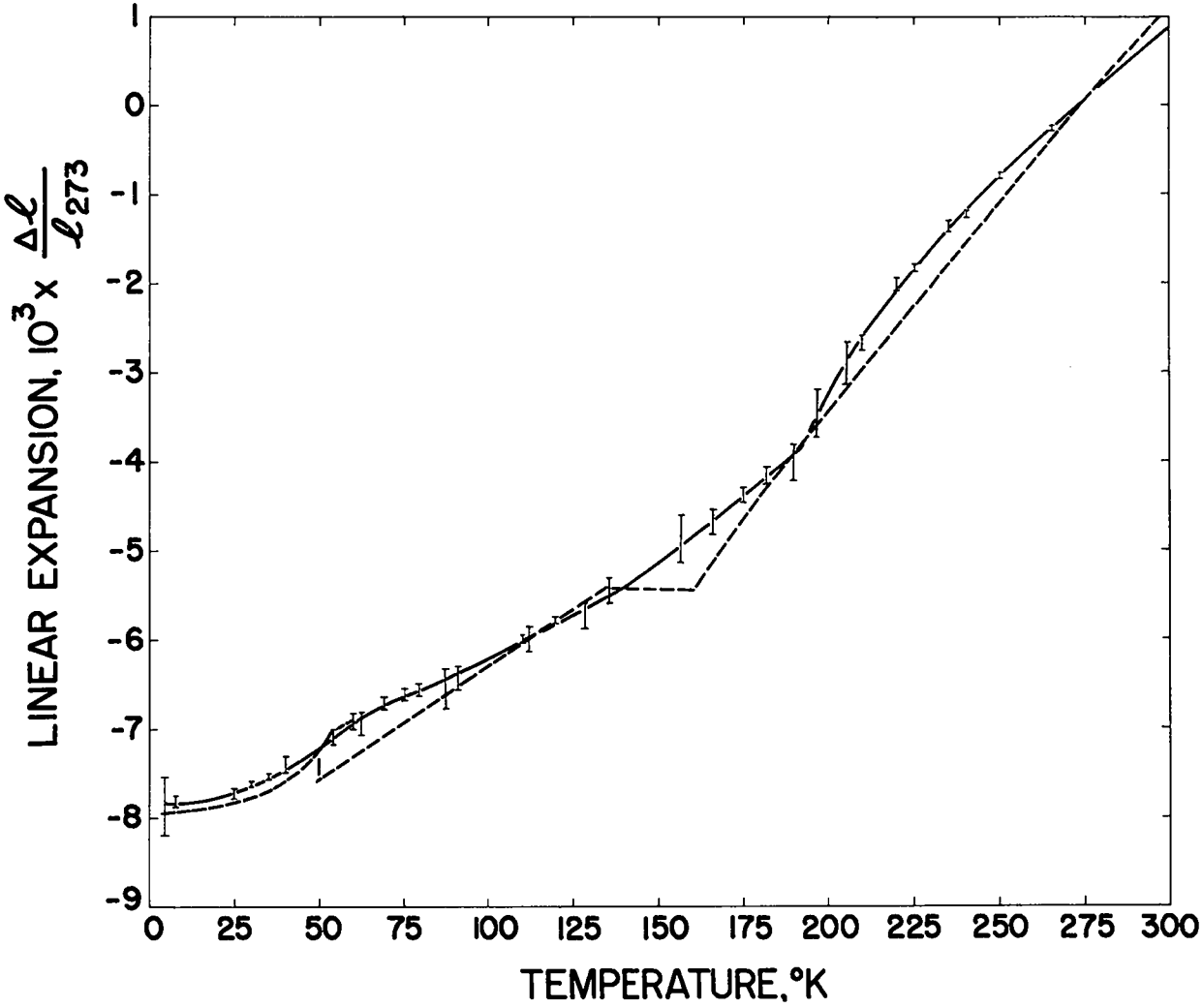

Fig. 4. Thermal expansion of a plutonium specimen with 600 ppm iron content relative to fused quartz (solid line). Dashed curve represents data for the normal purity specimen.

$$C = 7.5407446 \times 10^{-8}$$

$$D = -1.1509282 \times 10^{-10}$$

$$\sigma = \text{standard deviation} = 2.9 \times 10^{-5}$$

The temperature coefficient of thermal expansion, α, can be calculated for any temperature T by differentiation of the above equation.

4.5 Least Squares Equation for Linear Expansion of Plutonium Metal Below 273°K

The thermal expansion data for normal purity plutonium was also submitted for least squares analysis utilizing machine calculations. Because of the offset observed at ~50°K and the region of zero coefficient of linear expansion (between 135°K and 160°K), the data were divided into three temperature regions. The equations for these three regions were found to be as follows:

Temperature Range: 2°K to 55°K

$$\Delta l_T = l_{273} (A + BT + CT^2)$$

$$A = -7.9421680 \times 10^{-3}$$

$$B = -6.4305347 \times 10^{-6}$$

$$C = 4.1447317 \times 10^{-7}$$

$$\sigma = 1.3 \times 10^{-4}$$

Temperature Range: 50°K to 135°K

$$\Delta l_T = l_{273} (A + BT)$$

$$A = -8.8183670 \times 10^{-3}$$

$B = 2.5303415 \times 10^{-5}$

$\sigma = 6.4 \times 10^{-5}$

Temperature Range: 160°K to 273°K

$\Delta l_T = l_{273} (A + BT)$

$A = -1.3240679 \times 10^{-2}$

$B = 4.8509769 \times 10^{-5}$

$\sigma = 1.6 \times 10^{-4}$

5. DISCUSSION

5.1 Experimental Results

The thermal expansion of plutonium metal has been studied below room temperature by other workers.[2,3] Elliott and Tate[2] cooled an impure specimen of plutonium (730 ppm combined iron and nickel content) down to 93°K. Their value for linear contraction at 93°K falls 2.9% above the dashed curve of Fig. 3. Cramer et al.[3] used a shell of high-purity plutonium in later measurements. Their value of linear contraction for the same temperature falls 2.2% below the solid line of Fig. 3.

It should be explained that the room temperature phase of plutonium metal is anisotropic,[8] and, therefore, the values quoted in this paper and by the other workers are average values of contraction in the three crystallographic directions. A great deal of scatter could thus be expected in results obtained with different specimens of even the same purity.

It should also be noted that the solid curves given in Figs. 3 and 4 represent equilibrium values wherever possible. If, at any temperature below 160°K, heating at a continuous and constant rate was undertaken, the curve would tend to approach the dashed curve of Fig. 3 and continue upward near that curve as the temperature increased toward room temperature.

An examination of the above least squares equations for the linear expansion of plutonium metal shows the temperature coefficient of thermal expansion, α, to be constant between 50°K and 135°K and also between 160°K and 273°K. From the shape of the curve of Fig. 3, it is evident that the temperature coefficient, α, is discontinuous at 135°K and 160°K, with α being essentially zero between these two latter temperatures.

Jacobs and Goetz[9] have shown a similar type of temperature coefficient of thermal expansion curve for the anisotropic metal bismuth. The exception is that the temperature coefficient, α, of bismuth does not drop to zero in the temperature region between the discontinuities.

The compressibility of α-plutonium was studied by Bridgman[10] up to 100,000 kg/cm^2 in order to find any indication of new important transitions. The plutonium studied by Bridgman was wartime material and probably of a quality comparable to that of Elliott and Tate[2] which had a very high iron and nickel content. His work showed irregularities which were not inconsistent with a small reversible transition having a volume change of no more than 1%. The reversible volume change

indicated by thermal expansion at ~50°K is very small, percentagewise.

5.2 Correlation of Thermal Expansion Results with Other Physical Measurements

The slight offset in thermal expansion observed in normal plutonium in the range of 47°K to 52°K, when cooled extremely slowly, appears to be related to the heat capacity peak observed in high-purity plutonium at 47°K.

The thermal expansion behavior between 90°K and 165°K, when coupled with the electrical resistivity behavior[11] in this same temperature region, would appear to confirm the spin-disorder effects in plutonium, which are probably due to antiferromagnetism.

The approximately zero coefficient of thermal expansion over the range of 135°K to 160°K, as shown in Fig. 3, apparently has its origin in ordering phenomena. The linear contraction which would normally occur in cooling below 160°K must be opposed by an ordering expansion to give a net contraction which is almost zero. From specific heat measurements, it would appear that the temperature region of approximately zero coefficient of thermal expansion is above the suspected antiferromagnetic Curie point of 123°K.

The length of time required to get the equilibrium curves of Figs. 3 and 4, and the effect of impurity, i.e., iron, on the thermal expansion offset at ~50°K, explain the anomalous specific heat behavior with the appearance of clean-cut peaks at 47°K and 123°K[1] under certain processing conditions and the almost complete absence under

others. Unless the specimen was relatively pure and clean and was cooled in a manner that would permit maximum conversion to some other unspecified state(s), only well-defined heat capacity peaks would appear under conditions of adiabatic self heating. Since the thermal expansion specimens could be held at fixed temperatures until equilibrium conditions were attained, normal purity (as opposed to high-purity) specimens could be expected to show offsets, etc., and confirm the heat capacity behavior observed with high-purity material. It had been observed by Sandenaw and Gibney[11] that it took at least 24 hours for consistency in thermal conductivity measurements with plutonium at temperatures below 200°K. The time effect noted in thermal expansion studies verified this observation.

The thermal expansion curve of Fig. 3 also appears to confirm the observed width of the heat capacity peak with high-purity plutonium at 123°K. Previous to thermal expansion measurements, it had been impossible to understand why the minimum in heat capacity following this peak did not occur until a temperature of 155°K was reached.

It must be concluded from the shape of the curve for thermal expansion of plutonium metal, as shown in Fig. 3, that a different mechanism must be behind each of the noted heat capacity peaks. The change in slope of linear expansion in the case of plutonium metal with a 600 ppm iron content, as shown at 193°K in Fig. 4, should be reflected in the heat capacity of specimens having an appreciable iron content. Such an effect has been noted.[1]

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