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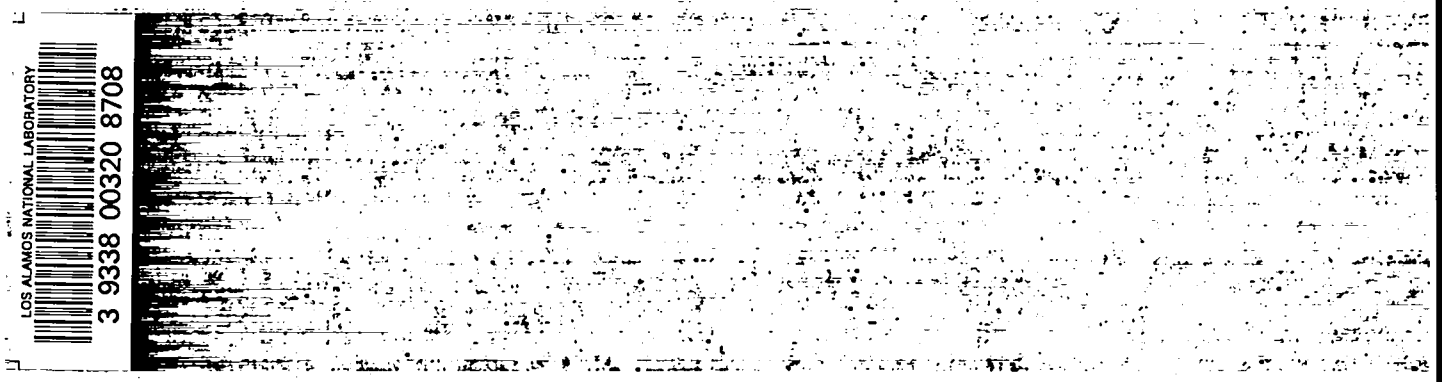
HEAT CAPACITY OF PLUTONIUM METAL BELOW 420°K



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HEAT CAPACITY OF PLUTONIUM METAL BELOW 420°K

by

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ABSTRACT

The heat capacity of plutonium as a function of temperature below 300°K is represented by curves and least-squared equations for specimens of different purities and isotopic contents. Values of the electronic contribution coefficient, the Debye characteristic temperature, and energy density of states are reported, together with entropy and enthalpy up to 298°K and also at 420°K. A figure showing the heat capacity behavior between 355°K and 420°K is also given. Anomalies in the heat-capacity curves are discussed, evidence from other types of experiments is presented to confirm their existence and significance, and possible explanations for them are considered.

ACKNOWLEDGMENTS

Thanks should again be given to those people previously credited for help given in checking out two calorimeter designs and determining the heat capacity of copper below 300°K.

In addition, we desire to thank the following people of the Los Alamos Scientific Laboratory: L. H. Treiman for calorimetry; Lorene L. Sturgess and Frank J. Dunn for mass spectrographic data; E. M. Cramer for metallographic analysis of specimens and for density determinations; E. F. Steigelmann (summer Laboratory employee) for assistance in measurements and calculations; Group CMB-11 for high purity plutonium specimens and results of chemical analyses; and Group T-1 for assistance in machine calculations.

1. INTRODUCTION

A thermally isolated plutonium specimen will experience a rise in temperature as a result of self heating due to radioactive disintegration. Since the rate of heat generation per gram of plutonium can be assumed to be constant, the rate of rise in temperature is dependent upon its specific heat. This property of plutonium can be utilized as a means for determination of its specific heat. Gibney and Sandenaw[1] first proved the feasibility of the method about ten years ago, when measurements of specific heat were made in the temperature range of 130°K to 420°K. Covering this range of temperature (T) incidentally allowed determination of the heat of the α- to β-phase transition.

More recently the authors returned to this problem in the hope of determining the heat capacity (C_p) of plutonium over the entire temperature range from 4°K to 900°K. Anomalous behavior was immediately discovered when specimens were cooled below the temperature of boiling liquid nitrogen; specific heat results were not reproducible. A multiplicity of spikes (or humps) was found in the C_p vs T curve; and by varying the precooling treatment, these could be shifted in temperature or almost made to disappear. The enthalpy (H) was found to be remarkably constant, regardless of the location or height of the peaks.

Considerable effort and a great deal of time was spent in attempts to get reproducible heat capacity curves. Various sizes and shapes of plutonium specimens were checked and material of varied purity was examined.

2. SPECIMEN DESCRIPTION

Two of the four specimens checked in the heat capacity calorimeters were cast from what has been described by Jette[2] as high-purity plutonium. The other two were machined from normal-purity material.

Specimens normally used in this apparatus were right circular cylinders 3/4 in. in diameter and 3/4 in. high. However, the possibility was suggested that, because of self-heating, massive plutonium specimens might not be cooled uniformly throughout their volumes by immersion in boiling helium. It was felt that, if an appreciable temperature gradient did exist within the specimen, it could be reduced by shortening the heat conduction path from center to surface, and that this would be reflected by a change in the experimentally determined heat capacity at low temperature. Accordingly, one of the cylindrical normal-purity specimens was checked twice over the temperature interval ~4°K to 300°K; then a 3/8 in. diameter hole was drilled through it along its axis and the runs repeated. No significant differences in results were observed, and so it was concluded that temperature uniformity was not a problem. As an added check, a plutonium specimen (normal-purity No. 2) was formed in the shape of a thin washer. This specimen was checked only in the temperature region of ~4°K to 60°K to confirm completeness of cooling of

larger solid specimens. Any differences due to cooling should have been detectible in the very low temperature heat capacity data, but none was detected.

Table I gives the purity, density, rate of heat generation, isotopic content, and dimensions of the four test samples. The isotopic analysis was made by a mass spectrograph, and heat generation was determined calorimetrically. One g/cal (mean) was considered as equivalent to 4.186 joules (absolute).

The heat capacity curves, as determined, appeared to be sensitive to impurities as well as to previous specimen history and processing. For this reason, major impurity elements are listed in Table II in parts per million. Only those elements present which differed in analysis by 5 ppm (or more) between normal- and high-purity specimens are tabulated.

3. EXPERIMENTAL DETAILS

3.1 Apparatus

Two sets of apparatus used in making the heat capacity measurements on plutonium below 300°K have been described by Sandenaw.[3] Only results obtained with the apparatus which was suitable for cooling with liquid helium will be given in this report. This apparatus was designed so that the test specimen could be cooled by direct contact with liquid helium or other liquefied gas.

Plutonium metal oxidizes very readily and is considered hazardous because of its α-emission and bone-seeking properties. Contamination of apparatus, particularly when a specimen was cooled directly in a

TABLE I

Description of Specimens

Specimen	Wt. % Pu	Density (g/cm^3)	Heat Generation (mw/g)	Isotopic Content (at. %) 239	240	241	Height (in.)	Diam. (in.)	Hole Diam. (in.)
HP No. 1	99.96	19.59	2.2248	95.36	4.39	0.24	0.75	0.75	-
HP No. 2	99.96	19.59	2.2248	95.37	4.40	0.24	0.75	0.75	-
NP No. 1	99.90	19.44	2.2900	94.63	5.03	0.34	0.75	0.75	none and 0.375
NP No. 2	99.89	19.50	2.2911	94.60	5.07	0.34	0.10	0.75	0.250

TABLE II

Impurity Elements in Plutonium Specimens (ppm)

Specimen	Mg	Ca	Al	Si	Ni	Fe	Cr	C
HP No. 1	< 5	5	< 5	40	< 20	70	< 30	137
HP No. 2	< 5	5	< 5	30	30	70	< 30	137
NP No. 1	80	10	10	75	160	200	30	205
NP No. 2	30	5	20	100	130	520	80	55

liquefied gas, was a problem. This was solved by furnishing the material with a thin but impervious nickel coat and then inserting the cylindrical specimens in containers made from oxygen-free high conductivity (OFHC) copper. Thermocouples used for measuring temperature were fastened to the copper, and the nickel-coated plutonium specimen was lightly spring-loaded against the copper jacket.

Details concerning the controllers, recorders, and cobalt-gold alloy vs copper thermocouples used for measuring temperature have been given elsewhere.[3]

3.2 Experimental Procedure

A slight overpressure of dried helium gas was maintained in the calorimeter while liquid nitrogen was added to the space surrounding the "canned" test specimen of plutonium. This was done to prevent condensation of moisture on the specimen and inner walls of the dewar during the transfer of the nitrogen. Initially, the liquid nitrogen was added merely to precool the specimen before continuing the cooling with liquid helium, and the liquid nitrogen was removed before introduction of liquid helium. It was soon found, however, that results for the heat capacity of plutonium at low temperatures under these conditions were irreproducible. A series of heat capacity spikes often appeared, and these would usually shift in temperature from run to run - or they might simply disappear.

Other experiments undertaken later indicated that cooling to ~48°K and holding for several days in the range of 48°K to 63°K would allow

near completion of what was suspected to be an antiferromagnetic transition. Therefore, the final procedure was to cool the specimen slowly to 80°K in the presence of 15 to 20 mm of helium exchange gas. An excess of liquid nitrogen was then added and pumped to an indicated temperature of 48°K to 50°K, freezing the nitrogen. After several hours the nitrogen changed back from solid to liquid, and pumping was repeated. This cycling was continued for periods ranging from 2 to 4 days before removal of the liquid nitrogen and addition of liquid helium. Liquid helium was normally held around the specimen for 15 to 20 minutes, then pumped to cool the specimen to approximately 1.9°K as indicated by the vapor pressure of the helium. The pumps were turned off, and the specimen was held in liquid helium for the remainder of an hour before the liquid helium was removed. The procedure followed in removing helium and starting the heat capacity run has been previously described.[3]

4. CALCULATIONS

Since the plutonium specimens were coated with nickel and contained in OFHC copper, it was necessary to correct the specific heat (or heat capacity) values for both the nickel and the copper. The existing heat capacity data of Busey and Giauque[4] for nickel were used in correcting the specific heat data. The heat capacity data used for OFHC copper were determined in the previously mentioned apparatus and have been reported.[3]

The heat capacity problem, in its entirety, was coded for solution by an IBM 704 Computer. Data required in the problem included: the specific heats of nickel and copper as functions of temperature, emf values of cobalt-gold alloy vs copper thermocouples as a function of temperature, the pertinent weights of copper, nickel, and plutonium, and the rate of heat generation and atomic weight of plutonium. The experimental data introduced consisted of thermocouple emf readings (in microvolts) at specified times, taken from a recorder chart. From this information the IBM 704 calculated the average temperature and the rate of temperature rise during specific time intervals by interpolation of the emf-temperature data previously fed into the machine. The copper and nickel specific heat data were then interpolated for each of these average temperatures. The solution printed by the machine listed average temperature, rate of temperature rise, and specific heats of copper, nickel, and plutonium for each of the chosen time intervals. This was repeated step-wise for the entire temperature range covered.

A second IBM 704 calculation converted specific heat of plutonium to heat capacity at each of these average temperatures, and integrated the C_p vs T data to give entropy, enthalpy, and Gibbs free energy. The calculation of enthalpy and entropy involved summation by a trapezoidal rule. The equations used in Fortran coding of the general problem for the IBM 704 Computer and results obtained for copper with these equations have been given by Sandenaw.[3] The thermodynamic data

obtained for copper at 298.15°K indicated that the method of calculation was adequate.

Numerical coefficients for the equations giving heat capacity of plutonium as a function of temperature were obtained by a least-squares treatment of data from several experimental runs, again by use of the IBM 704. In this problem the machine printed the sum of the squares of differences, and the standard deviations (σ) were easily calculated from these.

5. EXPERIMENTAL RESULTS

5.1 Heat Capacity Curves

It has been pointed out in the preceding discussion that values for the heat capacity of plutonium in the temperature range below 300°K were not reproducible until a method of specimen precooling was developed which appeared to allow maximum reproducibility.

The curve for the heat capacity of high-purity plutonium which was slowly cooled and held in the temperature range of 48°K to 76°K for 48 to 96 hours before cooling to 1.9°K, showed three major peaks. These peaks had very broad bases and appeared to be symmetrical about their crests. A curve of this type is shown as the predominately solid line of Fig. 1. The dashed sections of the curve represent ranges of greater fluctuations than usual in other temperature regions.

The data obtained with normal-purity specimen No. 1 appeared to be independent of pretreatment or cooling rate, and only the first (i.e., 31°K) spike was detected. These data are represented by the dashed

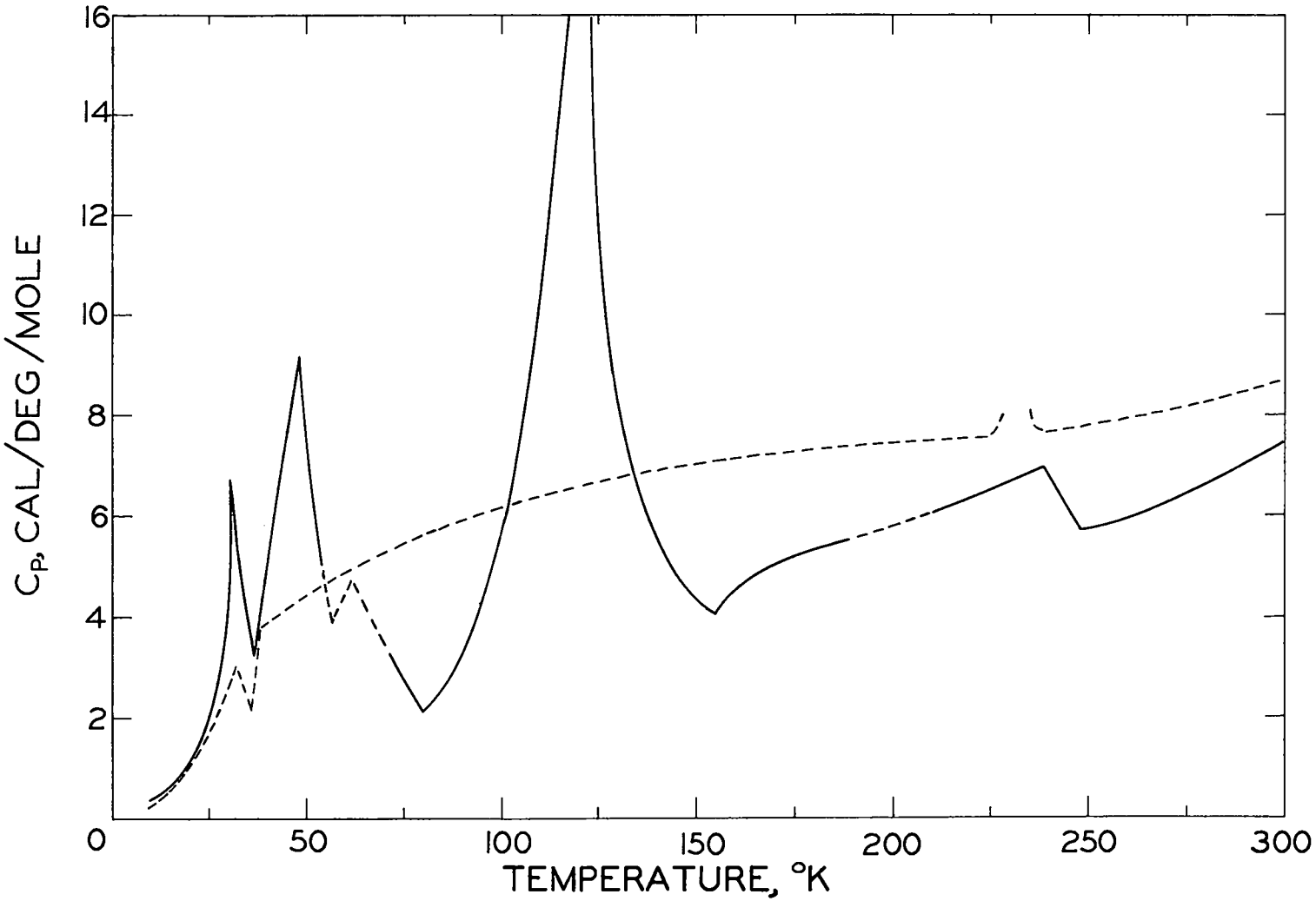

Fig. 1. Heat capacity as a function of temperature for high-purity (predominately solid line) and normal-purity (dashed line) plutonium specimens.

curve of Fig. 1. An indication of slight peaking was sometimes observed between 220°K and 240°K.

Different cooling rates and processing procedures with the high-purity specimens yielded curves intermediate between the two shown in Fig. 1. The confusion in the early measurements arose from the multiplicity of peaks. The major peak, with its crest at approximately 123°K, would sometimes appear instead as four to six spikes, the first occurring at a temperature as low as 100°K, and the last at 150°K to 160°K.

Fig. 2 shows the shape of the heat capacity curve at the α-β phase transition, as found by Gibney and Sandenaw.[1] This peak was much sharper than those found below 160°K. In the experiment which this curve represents, the α phase existed temporarily at a higher temperature than that of the transition, and then the temperature dropped back to remain constant for over two hours.

5.2 Least Squares Analysis of Data

It is understandable that a least-squares analysis of data obtained from specimens influenced so greatly by processing should show large standard deviations. Such an analysis of the data obtained in four runs with normal-purity specimen No. 1 yielded the following heat capacity equations in the temperature ranges indicated:

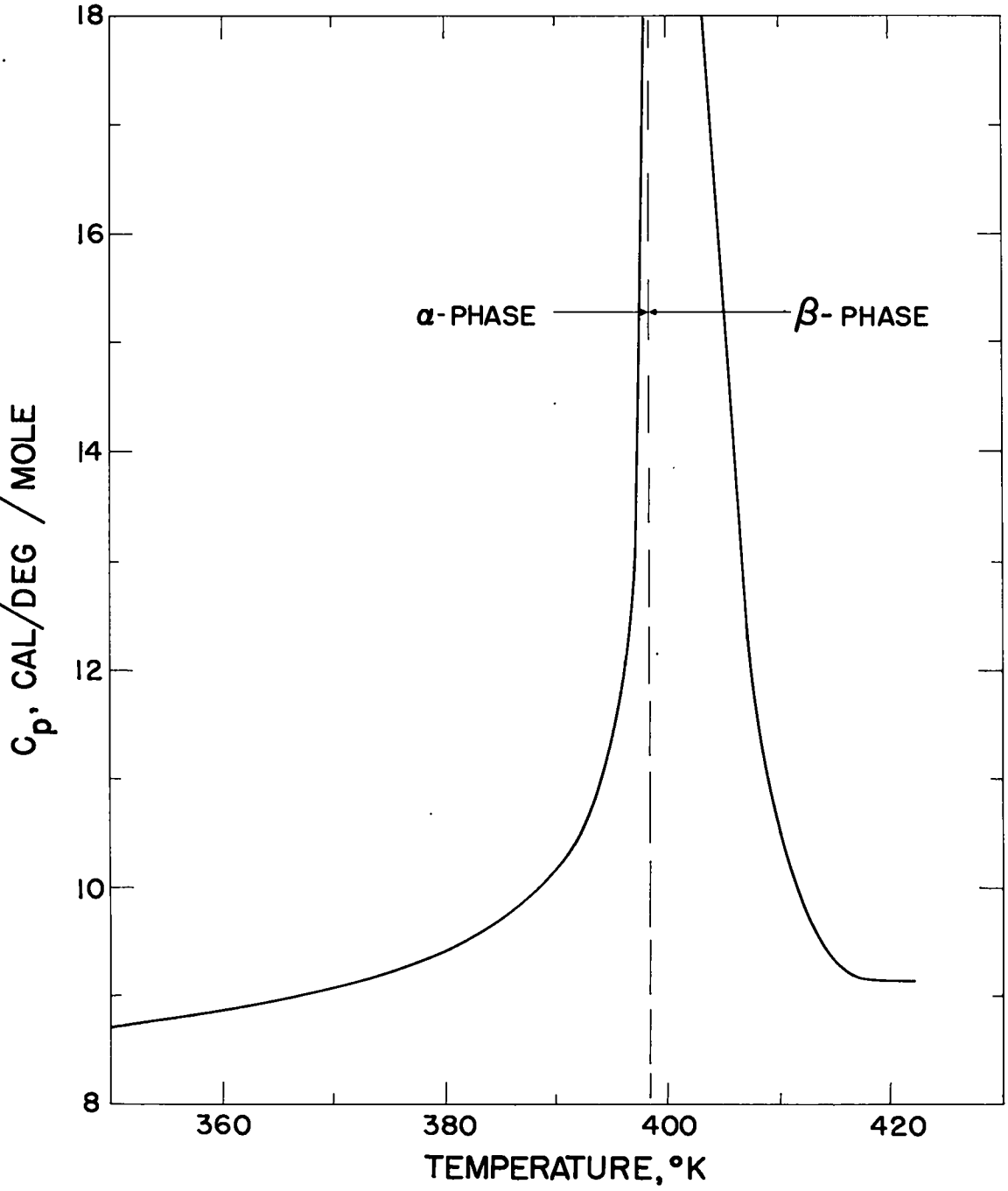

Fig. 2. Shape of heat capacity peak at the α-β phase transition.

Normal-purity No. 1 (4 runs)

Temperature Range below 21.25°K

$C_p = \gamma T + BT^3$

$\gamma = 1.1678 \times 10^{-2}$

$B = 9.276 \times 10^{-5}$

σ (standard deviation) = 0.066

Temperature Range 21.25°K to 31.81°K

$C_p = \gamma T + BT^3$

$\gamma = 2.2356 \times 10^{-2}$

$B = 7.1016 \times 10^{-5}$

$\sigma = 0.226$

Temperature Range 40°K to 298.15°K (Peak-free portion of curve for normal-purity specimen No. 1)

$C_p = A + BT + CT^2 + DT^3$

$A = 1.1282876$

$B = 8.2517711 \times 10^{-2}$

$C = -3.8530037 \times 10^{-4}$

$D = 6.4728553 \times 10^{-7}$

$\sigma = 0.226$

The very low temperature data from seven runs with the other specimens listed in Table I (i.e., excluding normal-purity No. 1) gave the following equation below 21.66°K:

Data from other specimens (7 runs)

Temperature Range below 21.66°K

$C_p = \gamma T + BT^3$

$\gamma = 2.0515 \times 10^{-2}$

$B = 8.4467 \times 10^{-5}$

$\sigma = 0.094$

5.3 Thermodynamic Properties

The general method for calculation of enthalpy and entropy has been discussed in Section 4. As was pointed out there, one of the listings from the IBM 704 electronic data processing machine was a table of calculated values of enthalpy and entropy for each given temperature. Heat capacity (C_p) and entropy (S) were assumed to be zero at 0°K. It was interesting to compare ΔH's and S's from different runs at various temperatures in the region below 300°K. The points chosen for comparison were at the minima following heat capacity spikes and also at 298.15°K. This comparison is shown in Table III. The integer in parentheses indicates in each case the number of values averaged. In this table the units of S are entropy units (cal/mole/deg) and of H are cal/mole.

Since entropy values were known after every small temperature change, it was easy to estimate the amount of extra entropy involved in each of the peaks shown in Fig. 1. Rather crude evaluations of this extra entropy are shown in Table IV.

TABLE III

Averaged Values of ΔH and S at Various Temperatures

Specimen	36.0°K to 36.5°K		85°K to 90°K		154°K to 156°K		298.15°K	
	S_T	$H_T - H_0$	S_T	$H_T - H_0$	S_T	$H_T - H_0$	S_T	$H_T - H_0$
HP No. 1	2.75(5)	65.0(5)	7.07(5)	328(5)	11.37(5)	834(5)	15.17(3)	1707(3)
NP No. 1	1.94(6)	43.6(6)	5.91(6)	283(6)	9.58(5)	728(5)	14.55(5)	1826(5)
HP No. 2 and NP No. 2	2.33(7)	55.3(7)	7.15(6)	338(6)	10.28(1)	764(1)	15.09(1)	1812(1)
Av. of all values	2.32(18)	54.1(18)	6.69(17)	316(17)	10.46(11)	779(11)	14.82(9)	1785(9)

TABLE IV

Calculated Extra Entropy in Heat Capacity Peaks

Temp. at Crest, (°K)	Extra Entropy (eu)
31	1.15
47	2.00
123	2.95

The heat capacity curve at the α-β phase transition for a rather impure plutonium specimen was shown in Fig. 2. Assuming that the entropy and enthalpy at 298°K were equivalent to the average found for the three specimens, it has been calculated that the entropy and enthalpy at 420°K would be 20.05 ± 0.40 eu and 3900 ± 100 cal/mole, respectively.

6. DISCUSSION OF RESULTS

6.1 Correlation of Heat Capacity Peaks with Other Physical Measurements

The electrical resistivity data[5] appear to offer confirmatory evidence for the three major heat capacity peaks observed in the C_p vs T curve of high-purity plutonium metal. The offset in the resistivity curve (Fig. 1, Reference 5) occurred at 31.5°K with one specimen and 27°K with the other, which is very close to the temperature observed for the first heat capacity peak, i.e., 31°K.

The dependence of electrical resistivity[5] upon holding time at ~48°K, can be surmised to be confirmation of the second heat capacity peak observed at 47°K; and the offset in linear expansion[6] noted in the temperature range 47°K to 52°K also appears to be contributory evidence for a heat capacity peak at 47°K.

The essentially zero coefficient of thermal expansion[6] over the short temperature range above 135°K, when coupled with the peaking of electrical resistivity at 105°K, would appear to be confirmation of the third heat capacity peak at 123°K.

The long times required for conversion to other states, as shown

in both electrical resistivity and thermal expansion measurements, help to explain the anomalous specific heat behavior with the appearance of clear cut peaks at 47°K and 123°K under certain processing conditions and absence under others.

6.2 Effects of Impurities on Physical Properties

Only the specimen designated as high-purity No. 1 gave the three well defined peaks shown in Fig. 1. This specimen was determined to be of higher purity than the others by both chemical analysis and metallographic examination. Although high-purity specimen No. 2 could also be classified as high purity on the basis of chemical analysis, metallographic examination showed the casting to be quite "dirty", with oxide skins and other unidentifiable metallic inclusions. Normal-purity specimen No. 1, which did not show heat capacity peaks at 47°K and 123°K, had a combined iron and nickel content of 360 ppm.

The thermal expansion curve for plutonium metal with a combined iron and nickel content of 150 ppm showed an offset at ~50°K. No offset was observed for plutonium metal having a combined iron and nickel content in excess of 600 ppm.[6]

The lowest residual resistivity[5] was found with the specimen containing the greatest quantity of ferromagnetic elements as impurities. Diverging resistivity paths were also found with this specimen.

The ferromagnetic elements, iron and nickel, when present in plutonium in amounts equal to or in excess of 360 ppm, thus gave evidence of effects on the low temperature specific heat, electrical

resistivity, and thermal expansion values. The over-all effect on thermal expansion and heat capacity appeared to be to delay the conversion to other states or to prevent conversion entirely.

6.3 Thermodynamic Properties

It should be noted that the maximum spread in the values of $(H_{298} - H_0)$ reported in Table.III was 8.5%. The maximum spread in values of S_{298} was 6.7%. The averaged values of $(H_{298} - H_0)$ of 1785 ± 60 cal/mole and S_{298} of 14.82 ± 0.35 eu appear to be quite good considering the divergent C_p vs T paths of different runs.

The extra entropy to be found in heat capacity peaks could be evaluated only crudely because of the influence of choice of a base line. It is believed that the extra entropy value mentioned previously for the peak at 31°K represents an extra spin (or magnetic) entropy. This is possible because of the non-vanishing spin which is a consequence of the incompletely filled electron shell(s) of plutonium.

The extra entropy of 2.95 eu for the peak at 123°K has a greater accuracy than the other values given in Table IV. This value probably corresponds most closely to $R\ln 4$.

6.4 Electronic Contribution Coefficient (γ) and Debye Characteristic Temperature (θ_D)

The electronic contribution coefficient (γ) to the heat capacity of plutonium was shown to vary from 116.8×10^{-4} to 205×10^{-4} by the least-squares analysis of the heat capacity data at low temperatures. The smaller of these two values yields a value for the energy density of states of

10.4 states per atom per electron volt, while the larger gives a value of 18.2 states per atom per electron volt. These are very high when compared to the published values for other elements. The magnitude of these calculated values of energy density of states seemingly indicates that there is considerable magnetic contribution all through this temperature range.

The values of the Debye characteristic temperature (θ_D) determined from the B term in the heat capacity equation, gives quantities of 171°K and 176°K, again comparing well with the value of 178°K calculated from the sound velocity measurements on plutonium by H. Laquer.[7]

6.5 Possible Explanations for Heat Capacity Peaks

The anomalies in the very low temperature heat capacity curves of cerium, praseodymium, and neodymium have been attributed by Parkinson et al.[8] to the presence of 4f electrons and Stark splitting of levels in the crystal field. Such an alternate explanation (splitting of levels) should possibly be considered for the 31°K heat capacity peak of the 5f element, plutonium.

The offset shown in the thermal expansion of plutonium at ~50°K is very similar in shape to the offset shown for lanthanum[9] at 583°K. The offset in lanthanum indicates a transition or phase transformation. It should be pointed out that the actual change in length of plutonium (dl/l_{273}) at ~50°K is many times that of lanthanum at 583°K. The proof of a phase change at ~50°K in the case of high-purity plutonium must, nevertheless, come from x-ray studies.

On the basis of the electrical resistivity behavior in the vicinity of 105°K, Sandenaw and Gibney[10] have suggested antiferromagnetic ordering of spin below this temperature. It appears that the major specific heat spike at 123°K could thus have its origin in spin disorder, i.e., in a transformation (on heating) out of the antiferromagnetic state. (The term described as spin disorder resistivity has been recently discussed in detail by B. R. Coles.[11]) The electrical resistivity peak at ~105°K, heat capacity peak at 123°K and change in slope of linear expansion at 135°K have all been claimed as indications of the same phenomenon. This spread in temperature between manifestations of the same property, as found by different physical measurements, is not unusual in antiferromagnetic materials. Ellefson and Taylor[12] found a 40°K difference between the temperature of the heat capacity spike in MnO and the temperature of a change in slope of the lattice constant of this same material. They also found a negligible temperature difference in the case of MnS.

6.6 Suggested Role of Electron Promotion

The similarities between manganese metal and plutonium metal are very striking. Both metals show peaks in the low temperature resistivity curves of their α-phase, room temperature resistivity values are high, and antiferromagnetic Curie points at ~100°K are established for manganese and are indicated for plutonium. The two metals have the same crystal structures in high temperature phases, i.e, face centered cubic, tetragonal,[13] and body centered cubic, although they do not occur in the

same order on heating. The high temperature susceptibility curves show similar swings and temperature dependence. In addition, the room temperature values for gram atomic susceptibility[14] are almost identical. There is a multiplicity of coordination numbers[15, 16] for the atoms found in the unit cell of their α phases. These coordination numbers run between 12 and 16 for both elements.

Because of the similarities between plutonium and manganese, it is interesting to speculate that plutonium metal consists of plutonium atoms of different electronic configuration and that this is reflected in the multiple specific heat peaks observed below room temperature and also in all physical properties measurable over a wide temperature range. The concept of the presence of atoms of different electronic states within the metallic elements of the 5f series is not new. Thewlis and Steeple[17] have used x-ray evidence to reach the conclusion that atoms with different electronic configurations occur in structures of β-uranium and α-neptunium.

The presence of atoms of different electronic configurations might be postulated as having its origin in properties of the 5f-6d electron separation. Fried and Zachariasen[18] have stated that the 5f-6d separation is considerably smaller than the corresponding 4f-5d separation (i.e., of the rare earth elements). Because of the very small energy separation between the 5f and 6d electron levels in plutonium, it is possible to bring about promotion or demotion of several electrons in this 5f element.

The extra entropy associated with heat capacity peaks at 31°K, 47°K, and 123°K was given in Table IV. (The values were considered to be crude because of an arbitrary choice of a base line for computation.) The extra entropy associated with each peak, in the order of increasing temperature, approximates Rln2, Rln3, and Rln4. The implication is intriguing if one considers the equation for magnetic entropy of Rln(2s + 1), given by Hofmann et al.,[19] where s is the spin per atom.

The inference is that plutonium is alloy-like in its character; also because of hysteresis noted in measurable physical properties in almost every solid phase, it may be that cooperative phenomena are responsible for a large part of the observed behavior, and that in certain temperature regions may originate through spin phenomena.

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