

1970

Low temperature specific heat of cerium and cerium-yttrium alloys

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PANOUSIS, Nicholas Theodore, 1942-
LOW TEMPERATURE SPECIFIC HEAT OF CERIUM
AND CERIUM-YTTRIUM ALLOYS.

Iowa State University, Ph.D., 1970
Materials Science

University Microfilms, Inc., Ann Arbor, Michigan

LOW TEMPERATURE SPECIFIC HEAT OF
CERIUM AND CERIUM-YTTRIUM ALLOYS

by

Nicholas Theodore Panousis

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of
The Requirements for the Degree of
DOCTOR OF PHILOSOPHY

Major Subject: Metallurgy

Approved:

Signature was redacted for privacy.

In Charge of Major Work

Signature was redacted for privacy.

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1970

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INTRODUCTION

Metallic cerium has been the topic of numerous theoretical and experimental studies originating mainly from its variable electronic and allotropic natures. It can exist in at least four different allotropic forms, three of which occur between room temperature and liquid nitrogen. At room temperature and one atmosphere pressure the stable allotrope is F.C.C. ($\underline{a} = 5.16\text{\AA}$) γ -cerium. Upon cooling a sample at normal pressure the γ -allotrope begins to transform to a second allotrope, β -cerium (D.H.C.P., $\underline{a} = 3.68\text{\AA}$, $\underline{c} = 11.92\text{\AA}$) at 250°K . Further cooling results in the remaining γ transforming to a third allotrope, α -cerium (F.C.C', $\underline{a} = 4.85\text{\AA}$) at 116°K . Unless special precautions are taken a sample of γ -cerium cooled to cryogenic temperatures at normal pressure will invariably contain a mixture of the α and β phases.

Presently there is considerable controversy concerning the electronic configuration of α -cerium (1,2,3,4,5,6). Positron annihilation experiments (1) suggest α -cerium has one $4\underline{f}$ electron, magnetic susceptibility measurements (3,4) indicate it has a partially filled $4\underline{f}$ band, while neutron diffraction results (5) suggest α -cerium has no $4\underline{f}$ electrons. In part, this uncertainty is due to the fact that essentially

all experiments performed on cerium were done on multi phase (α plus β) samples and not on pure single phase α -cerium.

Because of this lack of reliable data and great interest in the electronic nature of α -cerium a study of its low temperature specific heat was undertaken. At low temperatures the specific heat of most metals can be written as (7,8):

$$C(\text{total}) = C(\text{electronic}) + C(\text{lattice}) \quad (1)$$

where $C(\text{electronic})$ and $C(\text{lattice})$ are respectively the electronic and lattice contributions to the total specific heat. In the free electron approximation the electronic component is given by (7,8):

$$C(\text{electronic}) = (1/3)\pi^2 k^2 V N(E) T \quad (2)$$

$$= \gamma T \quad (3)$$

where k = Boltzmann's constant

V = molar volume

$N(E)$ = density of electronic states at the Fermi surface

γ = electronic specific heat constant.

The important feature to notice is the electronic specific heat is directly proportional to the temperature and the proportionality constant, γ , is in turn proportional to the density of electronic states at the Fermi surface. The derivation of Equation 2 shows $N(E)$, and hence γ , is an average property and so no details of the energy bands can be

explicitly obtained from the electronic specific heat. Nonetheless, γ is a useful parameter especially for comparing one metal to another (9,10).

The lattice contribution to the specific heat for metals at low temperatures is usually analyzed in terms of the Debye approximation which leads to (7,8):

$$C(\text{lattice}) = (12/5)\pi^4 R \left(\frac{T}{\theta} \right)^3 \quad (4)$$

$$= \beta T^3 \quad (5)$$

where R = gas constant

T = absolute temperature

θ = Debye characteristic temperature.

Substitution of Equations 3 and 5 into Equation 1 gives

$$C(\text{total}) = \gamma T + \beta T^3. \quad (6)$$

Within this model for $T \ll \theta$ a plot of C/T vs T^2 will be linear. The intercept at $T = 0^\circ\text{K}$ gives γ directly while θ is obtained from the slope. Thus, the first objective of this study was to prepare pure α -cerium and measure its low temperature specific heat thereby providing reliable experimental values for γ and θ to be used to support or refute current models.

The second objective of this work was a study of the D.H.C.P. β -allotrope. Magnetic susceptibility (3,4) and

neutron diffraction experiments (5) have established that β -cerium undergoes an antiferromagnetic transition at 13°K. Crystal field effects in β -cerium (11) based on specific heat measurements (12,13) have been considered, and an article by Gschneidner and Smoluchowski (6) considered among other topics the electronic structure of the β -allotrope. Unfortunately, as was the case for α -cerium, all measurements were in fact done on multi phase cerium samples and so interpretations based on these measurements are open to question.

To study the electronic and magnetic nature of β -cerium a two-fold approach was used here. First, an attempt was made to prepare pure single phase β -cerium. The second approach was to utilize the observations that yttrium, when added to cerium, stabilized the β -phase in cerium with respect to both the α and γ phases (14,15). The results of low temperature specific heat measurements on the β -stabilized Ce-Y alloys at several concentrations could then possibly be extrapolated to obtain values for the pure β -phase. A combination of these specific heat measurements with similar measurements on β -cerium should yield reliable information about the electronic and magnetic nature of the D.H.C.P. allotrope.

SAMPLE PREPARATION

Table 1 contains a chemical analysis of the metals used in this project.

 α -Cerium

As discussed above one cannot obtain single phase α -cerium by simply cooling γ -cerium from room temperature to cryogenic temperatures. Therefore, a three step technique based on the pressure-temperature diagram proposed by Gschneidner and co-workers (16) was used to prepare α -cerium, see Figure 1.

In the first step a well annealed sample of γ -cerium was compressed to 10,000 atmospheres pressure to convert it to the α -allotrope. Figure 2 shows the pressure cell. The piston-die combination was made of tungsten-carbide. A soft iron shell surrounded the die to protect the operator in case of failure of the die or piston. The die and shell were in turn inside a metal container which was filled with liquid nitrogen as required in the second step.

The second step was to cool the whole assembly, housing as well as sample, with liquid nitrogen while maintaining the pressure at 10,000 atmospheres. After reaching liquid nitro-

Table 1. Chemical analysis of components (impurity levels are given in atomic ppm)

Impurity	Ce ^a	Ce ^b	Y
H	417	972	353
C	-	-	180
N	40	30	76
O	551	1190	972
F	-	-	-
Mg	8	4	4
Al	6	6	30
Si	30	30	20
Ca	7	30	2
Sc	4	30	10
Cr	2	5	10
Mn	0.3	0.6	0.1
Fe	40	20	200
Ni	10	4	20
Cu	4	4	20
Zn	0.7	0.6	0.2
Y	20	160	M
La	10	5	1
Ce	M	M	0.6
Pr	10	70	0.2
Nd	50	200	1.0
Sm	N.D.	N.D.	N.D.
Eu	N.D.	N.D.	N.D.
Gd	40	140	4
Tb	<6	20	1
Dy	7	50	0.8
Ho	5	20	2
Er	10	20	1
Tm	0.1	0.1	N.D.
Yb	<1	0.5	N.D.
Lu	0.2	0.3	1
Ta	30	60	3
Th	40	50	1

M - Major component; < - Less than; N.D. - Not detected;
 - Not analyzed for.

^aCe used in preparation of α and β allotropes.

^bCe used in preparation of Ce-Y alloys.

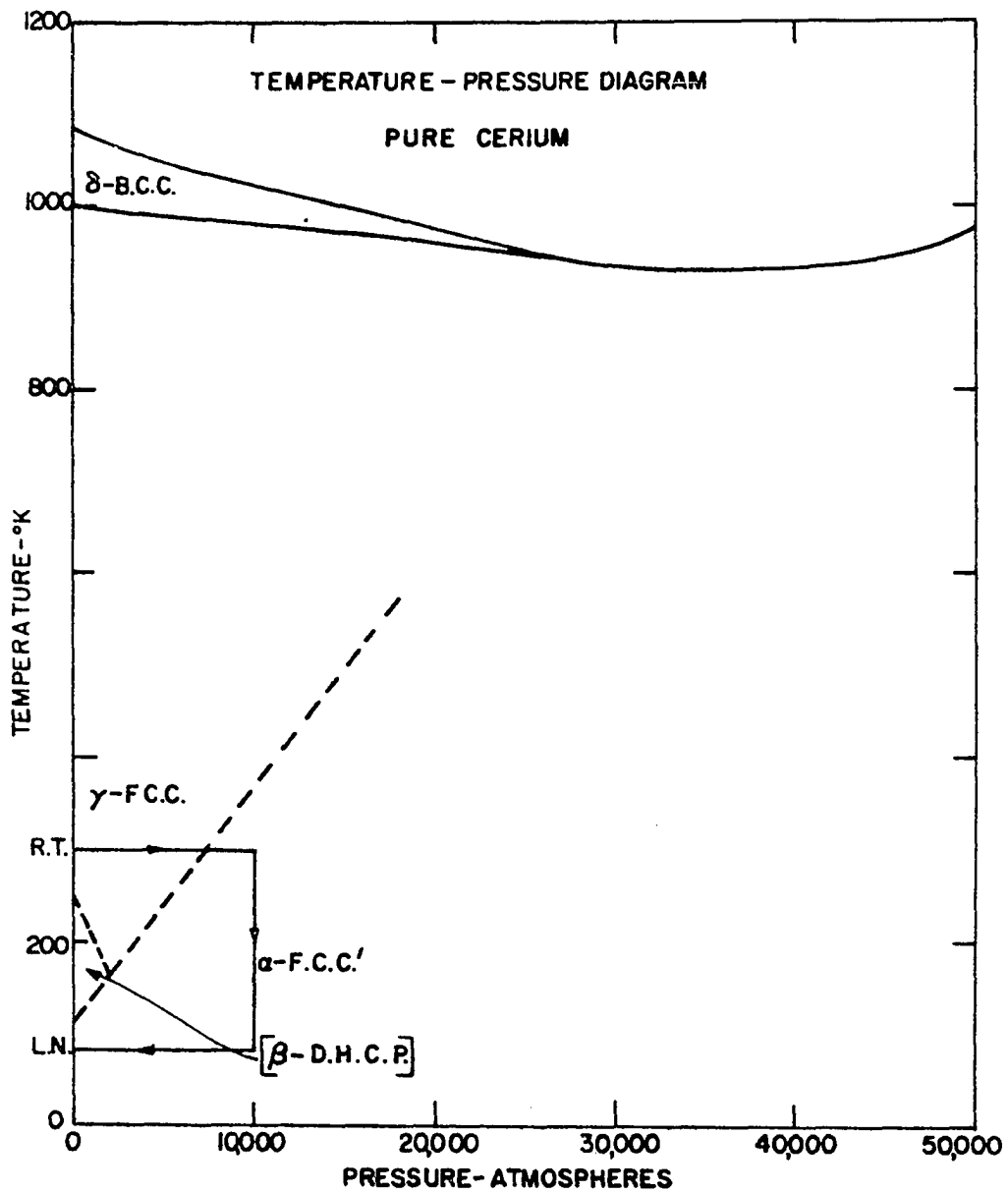


Figure 1. Temperature-pressure cycle to prepare α -cerium

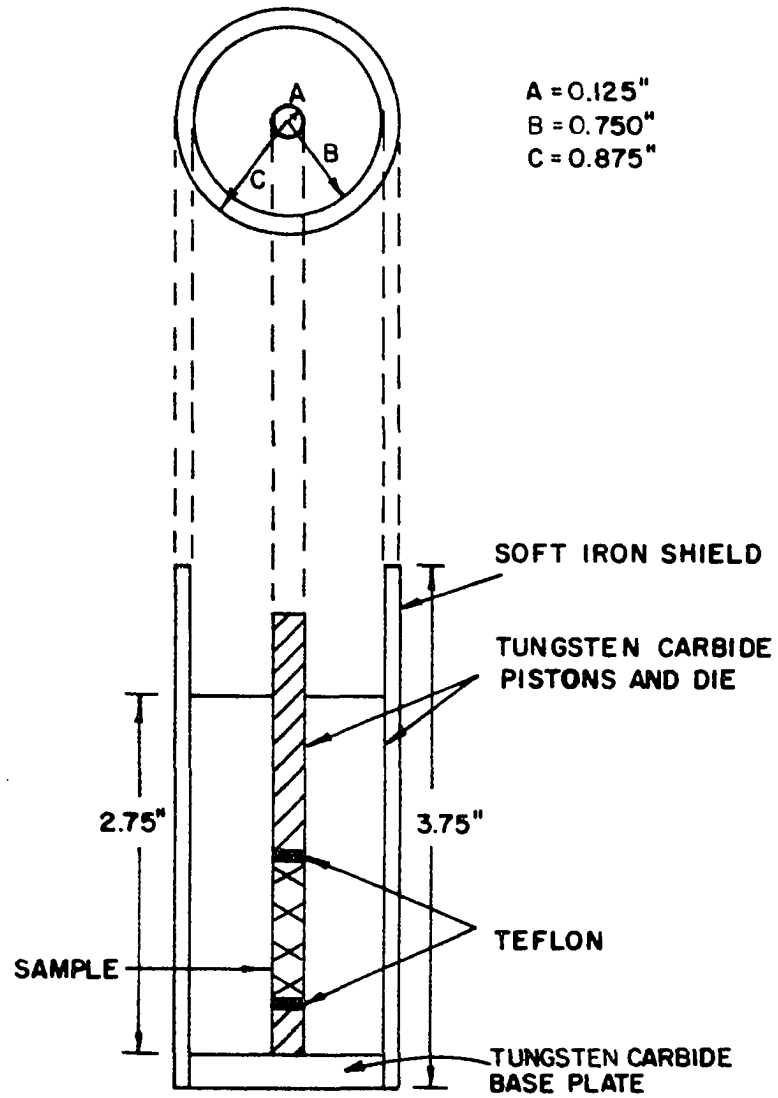


Figure 2. Details of pressure cell used to prepare α -cerium

gen temperature, the third step was to release the pressure. The sample was maintained at 77°K for loading into the calorimeter after which it was cooled to 4.2°K . This loading procedure is described in more detail in a latter section. Suffice it to say here that single phase α -cerium containing 0.25% β -cerium or less was obtained via this technique.

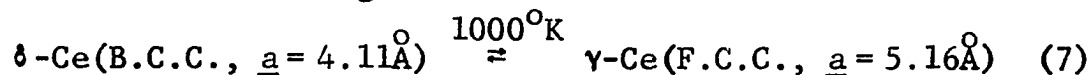
β -Cerium

The procedure used in the past to prepare β -cerium was to begin with a γ -cerium sample, cool it to cryogenic temperatures, then warm it back to room temperature. After this first cycle the sample would contain about 25-50% β -cerium with the rest γ -cerium. Further cycling as many as 100 times normally resulted in a maximum of only about 60-75% β -cerium the remaining being γ or α -cerium depending on the temperature. A 100% β -cerium sample was desired for the present study.

The technique used here in an attempt to prepare pure β -cerium was based in part on the work of Koch and McHargue (17). They found the degree of completion of the transformation $\gamma \rightarrow \beta$ was dependent on the original grain size of the γ -cerium. Specifically, they found that γ -cerium containing large grains (~ 5 mm average diameter) yielded more β -cerium

on cooling than did a γ -cerium sample containing small grains (0.005 to 0.1 mm average diameter). It therefore appeared reasonable that as large as possible grains should be prepared for a γ -cerium sample which should then be thermally cycled to induce the $\gamma \rightarrow \beta$ transformation.

Large grains of γ -cerium were prepared as follows. A cerium sample was melted in a conventional arc melter into the shape of a finger approximately 3" long and 5/16" in diameter. The sample was first sealed in a tantalum crucible and then in a quartz tube, and heated to 975^oK for 24 hours. It was then given a 5 step heat treatment to induce grain growth: (1) heated to 1025^oK for 12 hours, (2) cooled to 975^oK for 12 hours, (3) heated to 1025^oK for 12 hours, (4) cooled to 975^oK and held there for 10 days, (5) air cooled to room temperature. This method of grain growth utilizes the induced strain which results from thermally cycling cerium through the allotropic transformation occurring at 1000^oK.



Grain size after this procedure was 2-3 mm.

The sample was then cycled thirty times between room temperature and 4.2^oK to induce the $\gamma \rightarrow \beta$ transformation. Because of the sample's large grains and their preferred orientation

the relative amounts of the γ and β phases present could not be determined by conventional x-ray diffractometer techniques. Therefore low temperature dilatometry, a method described and used by Gschneidner and co-workers (16), was used to determine the relative amount of α and β present in the sample. These measurements indicated the sample was $91 \pm 5\%$ β phase with the rest α -phase. To date this is the highest β -phase fraction ever prepared in pure cerium samples.

β -Stabilized Ce-Y Alloys

For convenient reference the Ce-Y phase diagram (15) is reproduced in Figure 3. The six filled circles show the locations and anneal temperatures of the alloys. All six were prepared by melting weighed amounts of Ce and Y in a conventional arc melter. Contamination by air was kept to a minimum by handling and storing the metals and alloys in a dry argon atmosphere. After arc melting the alloys were sealed in Ta crucibles and quartz tubes and given the heat treatments summarized in Table 2.

As seen from the Ce-Y phase diagram, Figure 3, sufficient amounts of Y added to Ce results in the stabilization of β -cerium. It was felt the 96.1 a/o cerium alloy which was in the γ -stabilized region may be induced to transform to the

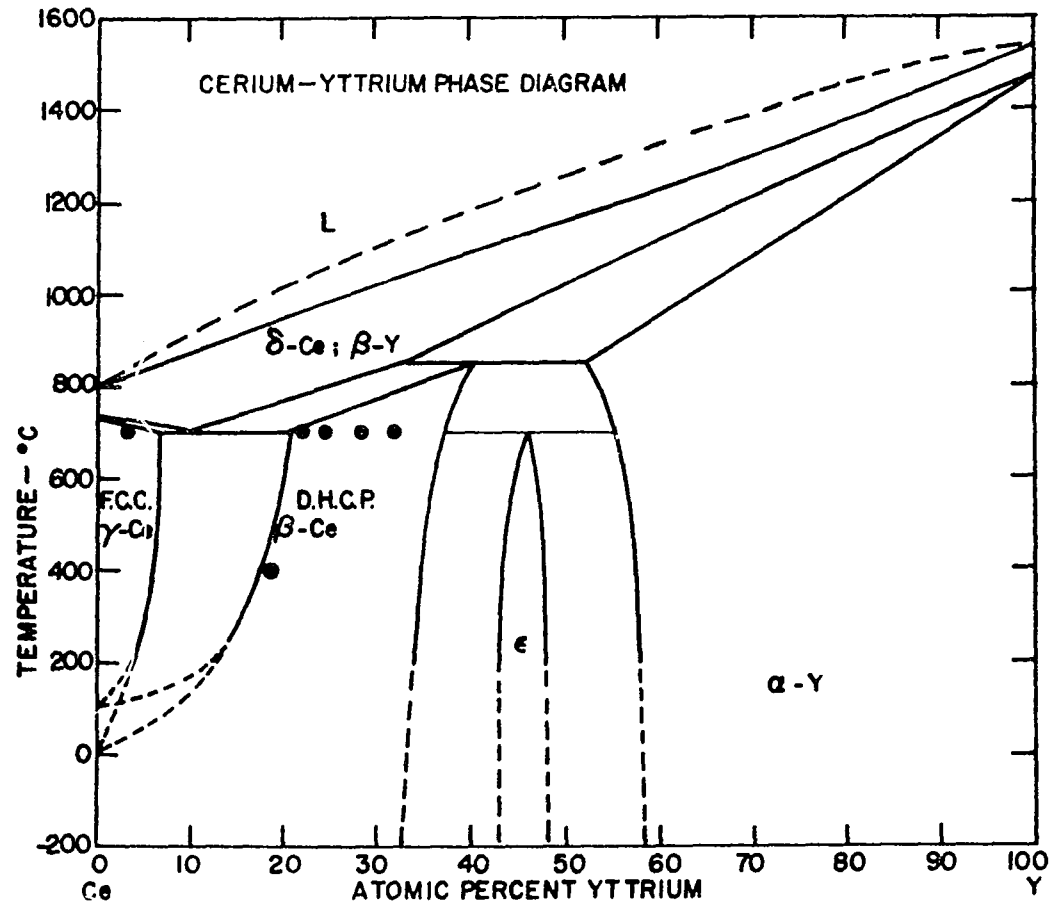


Figure 3. Cerium-yttrium phase diagram showing locations of alloys used in these experiments

Table 2. Summary of the anneal times and temperatures of the six β -stabilized Ce-Y alloys

Alloy (a/o Ce)	Anneal time (days)	Anneal temperature ($^{\circ}$ C)
96.1	68.9	700
82.3	74.9	400
78.2	61.1	700
75.6	40.2	700
71.7	52.1	700
68.6	60.9	700

β -phase by thermal cycling between room temperature and 4.2° K. To check this possibility the alloy was quenched to room temperature after its heat treatment then cycled 30 times between 4.2° K and room temperature. Examination by a conventional x-ray diffractometer showed the alloy was approximately 85-90% β -phase with the remainder γ -phase.

The other five alloys were air cooled to room temperature following their heat treatment and examined with the x-ray diffractometer. As expected from the phase diagram all five alloys were single phase D.H.C.P. to within a detection limit of $\sim 10\%$.

APPARATUS

An adiabatic calorimeter was designed and constructed for these experiments. In simplest form the operating principal was to thermally isolate a sample from its surroundings. A known amount of heat was supplied to the sample and the resulting rise in temperature was noted. The specific heat was then given by the ratio of the heat input to the rise in temperature.

Two modifications of the calorimeter were used in these experiments. First a special liquid nitrogen loading modification was required because the α -cerium sample had to be mounted in the calorimeter while at 77^oK. The second, called the normal modification, was used for the cases where the samples were loaded into the calorimeter at room temperature. The actual operating procedure as well as the methods of data acquisition and reduction are only briefly mentioned since they have been carefully described by R. R. Joseph (18).

Calorimeter, Normal Modification

Details of the normal modification are shown in Figure 4. The addendum consisted of a gold plated copper block to which were attached: 1) the sample heater, 1940 Ω (room temperature value) non-inductively wound manganin wire, 2) a germanium

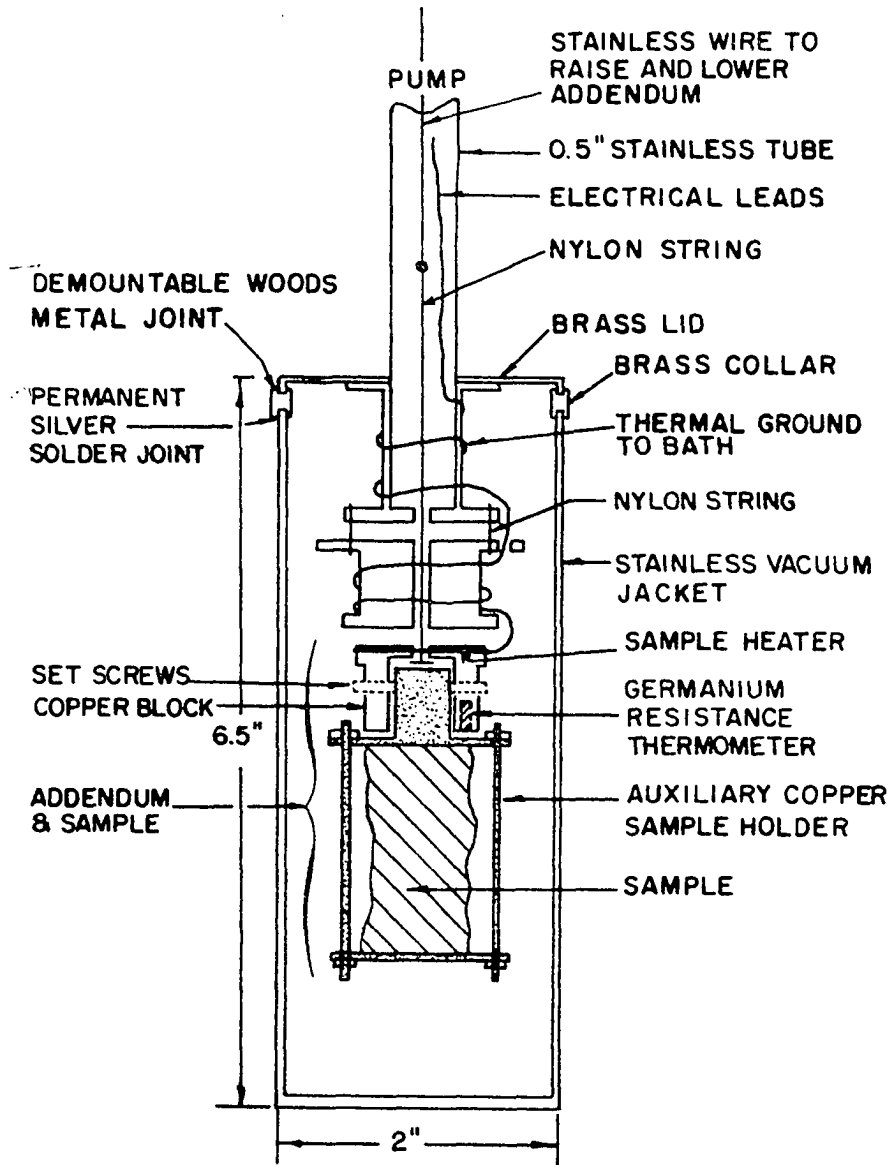


Figure 4. Details of the calorimeter, normal modification

resistance thermometer, 3) the gold plated copper auxiliary holder, and 4) five gold plated copper set screws to clamp the auxiliary holder into place. A stainless steel vacuum jacket surrounded the sample-addendum combination. Woods metal was used at the lid-jacket joint for convenient demounting.

To make a run the sample was cooled to 4.2°K by raising it into thermal contact with the liquid helium bath. After bath temperature was reached, typically one to five hours, the sample was lowered to break thermal contact and the run begun. Five to nine hours were usually required to complete a specific heat run.

Calorimeter, Liquid Nitrogen Loading Modification

The principal design requirement of this modification of the calorimeter was the capability of loading the α -cerium sample while it was under liquid nitrogen. As discussed in detail in an earlier section once α -cerium was prepared it had to be kept below about 180°K to prevent it from transforming back to the γ -phase.

Upon completion of the temperature-pressure cycle the α -cerium was drilled and tapped while under liquid nitrogen and then threaded onto a copper plug which was in turn clamped

into the copper block, see Figure 5. The intermediate copper plug was necessary because the larger thermal contraction of α -cerium with respect to copper caused the α -cerium sample to fall out of place when clamped directly to the copper block. Next the sample was immersed in liquid nitrogen which was contained in the stainless steel vacuum jacket. Because of the poor thermal conductivity of the stainless steel vacuum jacket it was possible to make either a soft solder or Woods metal connection at the lid-jacket joint while the sample was immersed in liquid nitrogen just one inch away! The final step was to pump out the liquid nitrogen and cool to 4.2°K.

Data Acquisition and Reduction

Data acquisition was basically a four step process. First, the sample temperature was measured. Second, two simultaneous operations were carried out: a) an electric current was supplied to the sample heater causing a rise in temperature, and b) an electric interval timer was started, see Figure 6. The third step was to end the heat pulse by simultaneously shutting off the electric current and interval timer. Fourth and last the increased sample temperature was measured. The procedure was then repeated for the next data point.

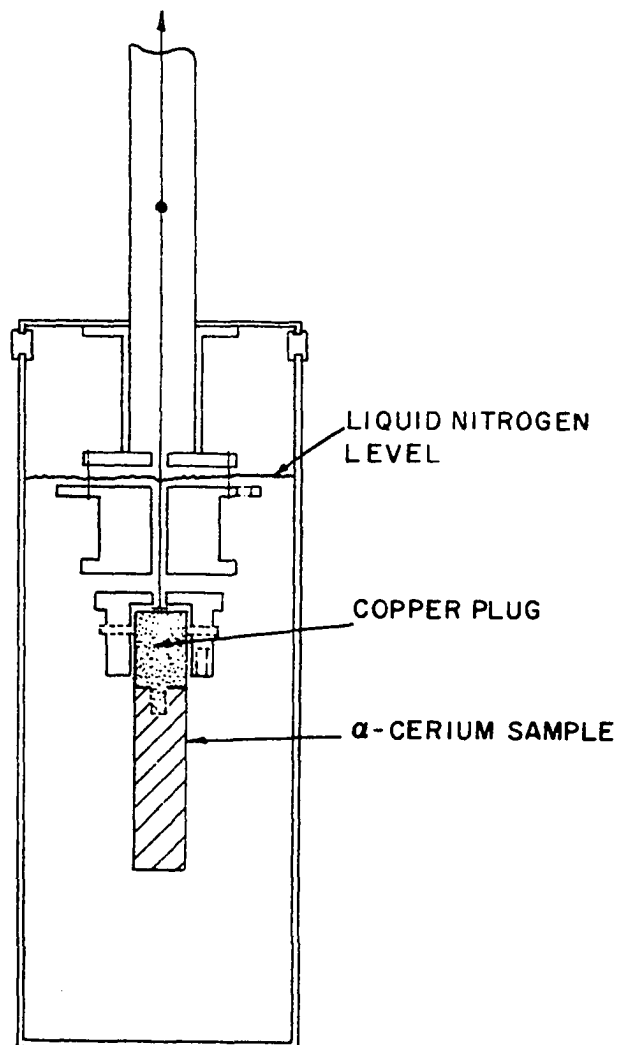


Figure 5. Details of the calorimeter, liquid nitrogen loading modification. Additional details in Figure 4

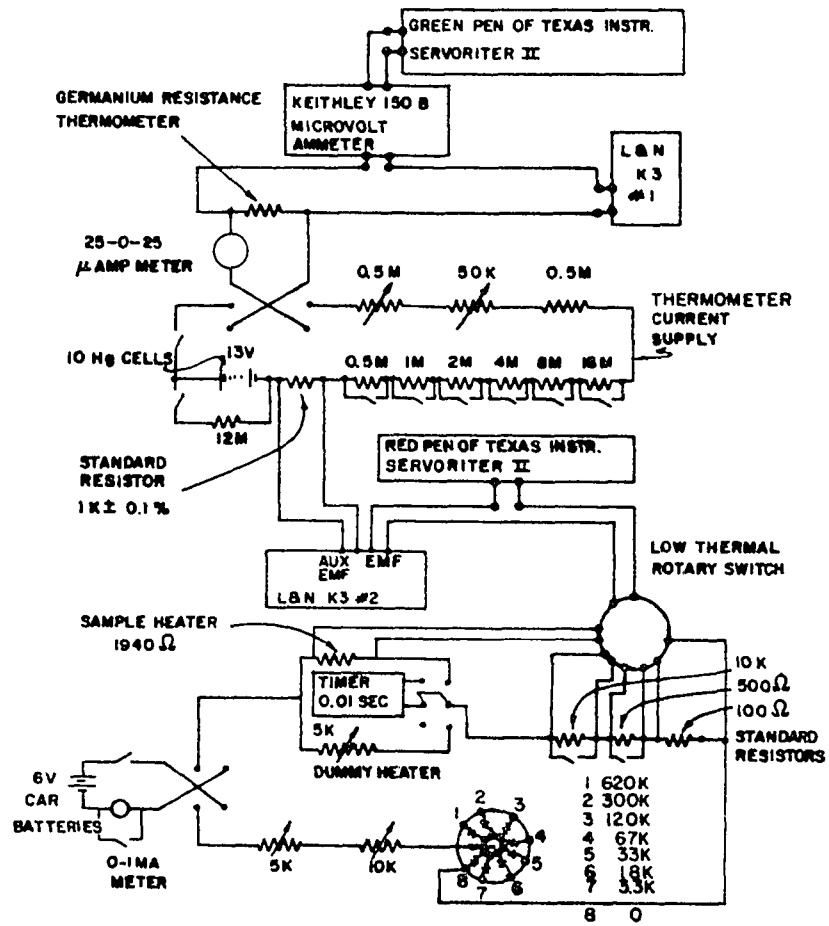


Figure 6. Calorimeter circuit diagram

Data reduction consisted of a calculation of the sample specific heat based on the following equation (all calculations were done on an IBM 360/65 computer):

$$CN = \frac{(I_H^2 R_H(T) + \Delta Q) \Delta t}{T_F - T_I} - C_{Add}(T) \quad (8)$$

where C = specific heat of sample

N = number of moles or gram-atoms of sample

I_H = heater current, values ranged between 0.1 to 2.0 ma

$R_H(T)$ = temperature dependent heater resistance, $R_H(T)$ was measured from 2.5°K (1710Ω) to 20°K (1732Ω)

$\Delta Q = 1/2 I_H^2 R_L$, a one percent correction for the heat generated in the electrical leads between the bath and the addendum, R_L is the resistance of this portion of the leads (19Ω)

Δt = elapsed time of heat pulse, typically 20-80 seconds, Δt and I_H were adjusted to give $\Delta T \approx T/25^\circ K$

T_F = temperature of sample after heat pulse, temperature was measured with a Solition germanium resistance thermometer which was calibrated against the T618 temperature scale (19)

T_I = temperature of sample before heat pulse

$C_{\text{Add}}(T)$ = temperature dependent addendum heat capacity

$C_{\text{Add}}(T)$ was measured between 2.5 and 20°K

Plots of C vs T and C/T vs T^2 were also generated by the computer.

Accuracy Check

The accuracy of the apparatus was checked by measuring the specific heat of a 1965 Calorimetry Conference copper standard. Two separate runs were made and the results were compared to the smoothed values (20,21) in Figure 7, where the points are the present results and the line is the best values for the 1965 Calorimetry Conference copper. An overall accuracy and precision of ~1% was indicated.

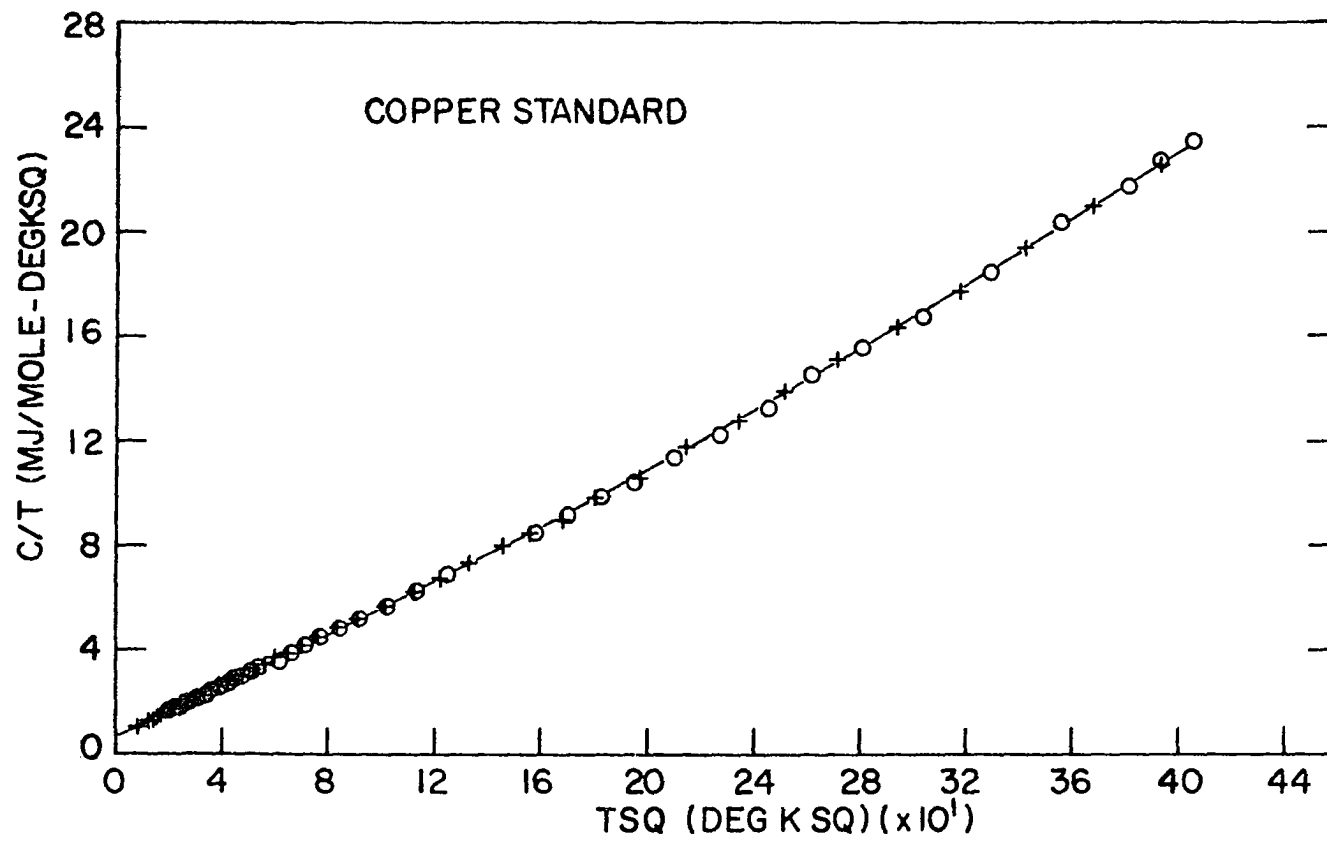


Figure 7. C/T vs T² plot for copper

RESULTS AND DISCUSSION

 α -Cerium

The specific heat of α -cerium between 2.5 and 20^oK is shown in Figure 8. The smooth data indicates the sample was free of the other cerium allotropes. Since β -cerium is known to magnetically order at about 13^oK (3,5) its presence would be indicated by a peak in the specific heat at 13^oK. We estimate we can detect the presence of approximately 0.25% β because of the large specific heat associated with the magnetic ordering of this phase. Figure 9 shows the standard C/T vs T² plot of the low temperature data which was least-squares fitted by computer to give $\gamma = 9.79 \pm 0.10$ (mj/mole-deg K²) and $\theta = 117 \pm 5^{\circ}\text{K}$.

These γ and θ values agree reasonably well with the high pressure (11 kbar) specific heat results of Philips, Ho, and Smith (22) who found $\gamma = 11.3$ (mj/mole-deg K²) and $\theta = 200^{\circ}\text{K}$. The large difference between the present θ value and that of Philips and co-workers is consistent with the observed increase in α -cerium Debye temperature with increasing pressure as reported by Vornov, Vereshchagin, and Goncharova (23). In fact the present value of 117^oK for the Debye temperature compares very well with the value of 118^oK as obtained by

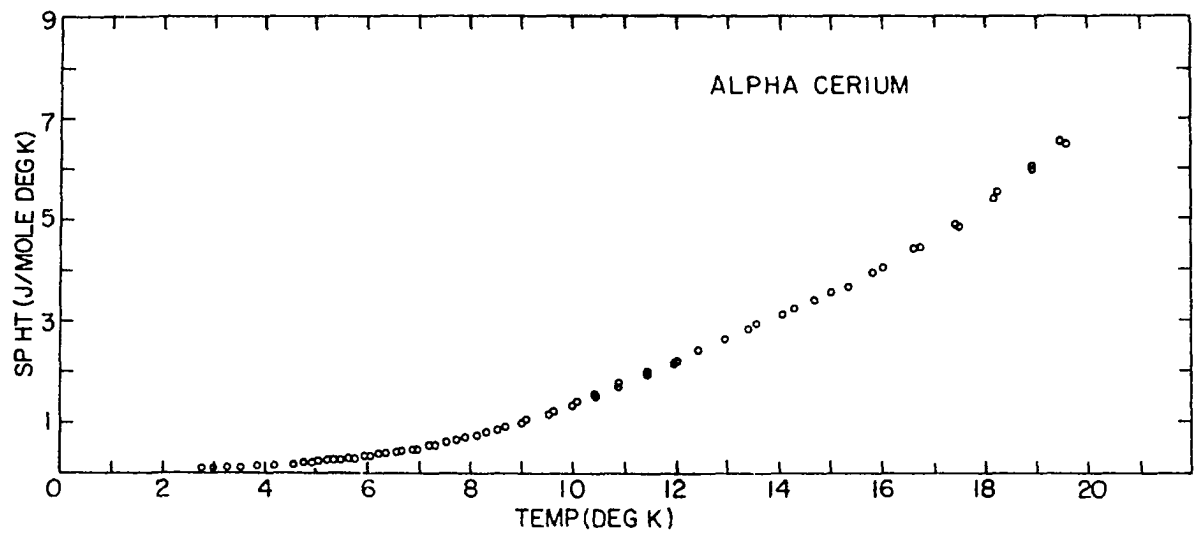


Figure 8. Specific heat vs temperature for α -cerium

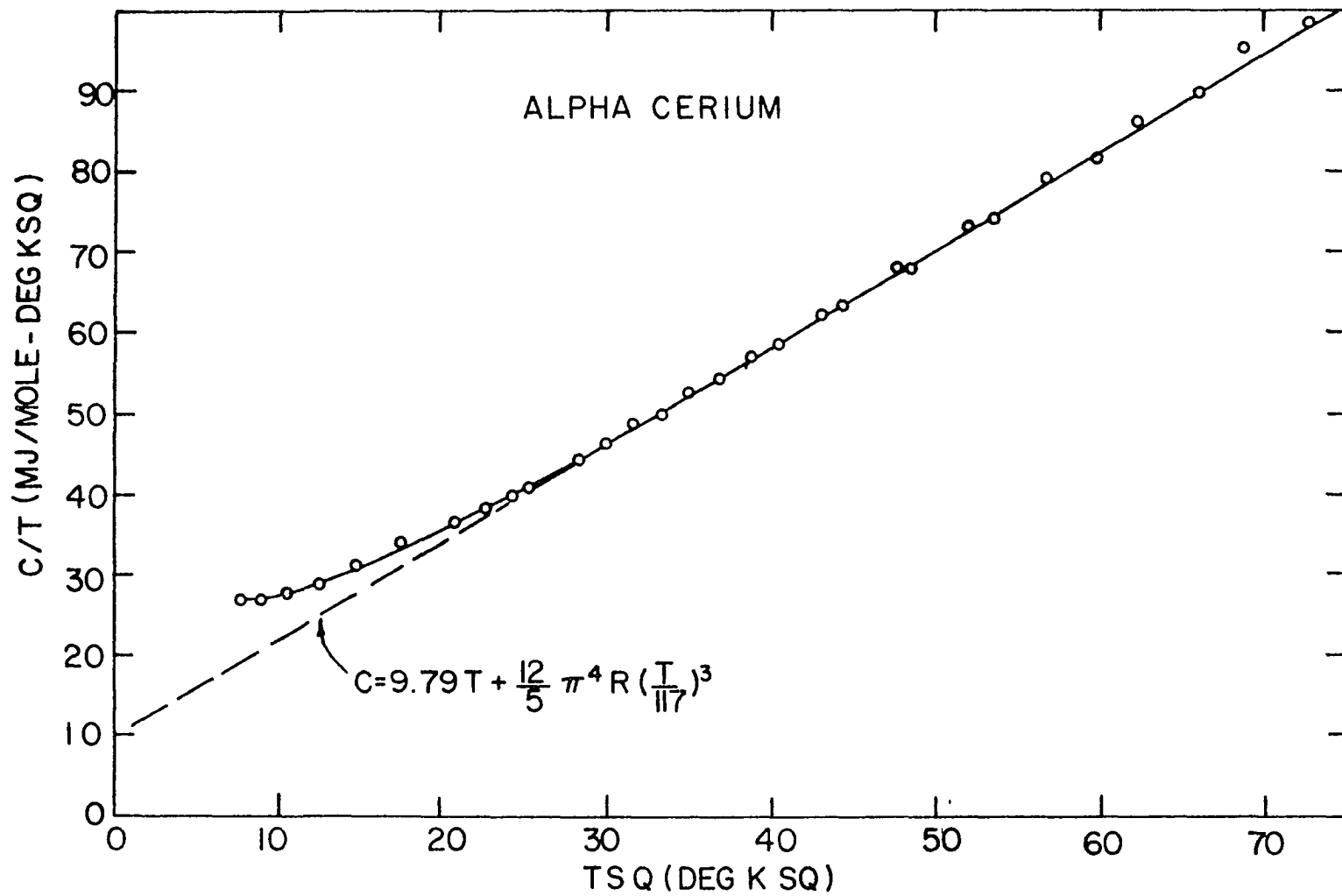


Figure 9. C/T vs T² plot for α-cerium

extrapolation to atmospheric pressure of the high pressure room temperature data of Vornov and co-workers.

The electronic specific heat constants as determined from Mukhopadhyay and Majumdar's (24) density of states values for α -cerium are 3.7 (mj/mole-deg K^2) for three s d electrons and 2.9 (mj/mole-deg K^2) for the four s d electrons. These values, respectively, are $2\frac{1}{2}$ and $3\frac{1}{2}$ times smaller than the observed value. Probably this is due to electron-phonon and electron-electron interactions which cause an enhancement of the observed electronic specific heat constant. This enhancement is somewhat larger than the factor of two observed for Sc (25), Y (26) and the heavy lanthanides (26) for which density of states values were calculated by using an APW method, the same method as used for α -cerium.

Other low temperature specific heat measurements on cerium have been on samples containing mixtures of the α and β allotropes (12,13,27). The values heretofore for the electronic specific heat constant and the Debye temperature for α -cerium were obtained by assuming a value for the β -phase and estimate of the amounts of α and β present. Values so obtained for α -cerium are open to serious criticism. Indeed γ values for α -cerium from 21.0 to 57.7 (mj/mole- $^{\circ}K^2$) have been summarized by Gschneidner (28).

Finally the C/T vs T^2 plot for α -cerium, Figure 9, shows positive curvature at the lowest temperatures. While the origin of this curvature is not known a few possibilities can be considered. First, magnetic ordering of the impurities present must be considered. Analysis of the samples before and after the measurements, Table 1, indicated a relatively low magnetic impurity content and a high, 99.9 atomic percent, purity cerium sample was used in these experiments. This sample analysis makes impurity ordering a doubtful cause of the positive curvature.

A second possibility is that a small amount of the β -phase was actually present in the sample. Since β -cerium magnetically orders at 13°K α -cerium could dilute the strength of the magnetic interaction and cause the β -phase to order at a much lower temperature. A sample which was a mixture of β plus γ cerium was run through exactly the same temperature-pressure cycle as described above and it was found to order at $\sim 13^{\circ}\text{K}$. Assuming the γ transformed to α while the β remained unchanged this separate run makes the β -impurity idea a doubtful origin of the observed curvature.

The last possibility considered here is simply that the α -cerium itself is undergoing a magnetic transition. This is

at least possible since some earlier investigators have attributed approximately 0.3 4f electrons to the α -phase (6). Further specific heat measurements to lower temperatures combined with magnetic susceptibility measurements should help explain this observation.

β -Cerium and β -Stabilized Ce-Y Alloys

Figures 10 through 16 show the specific heat results for a 91% β -9% α -cerium sample and the β -stabilized Ce-Y alloys. The first feature to notice is all six alloys showed magnetic ordering characteristic of β -cerium. Table 3 summarizes the ordering temperatures and Figure 17 illustrates the almost linear dependence of cerium concentration with ordering temperature.

Table 3. Summary of the ordering temperatures and phases present in the high β -cerium sample and the six β -stabilized Ce-Y alloys

Alloy (a/o Ce)	Ordering temperature ($^{\circ}\text{K}$)	Phase present
100	$12.8 \pm .1$	$\alpha+\beta$
96.1	$11.4 \pm .1$	$\alpha+\beta$
82.3	$8.5 \pm .1$	β
78.2	$7.7 \pm .1$	β
75.6	$6.9 \pm .1$	β
71.7	$5.9 \pm .1$	β
68.6	$5.05 \pm .1$	β

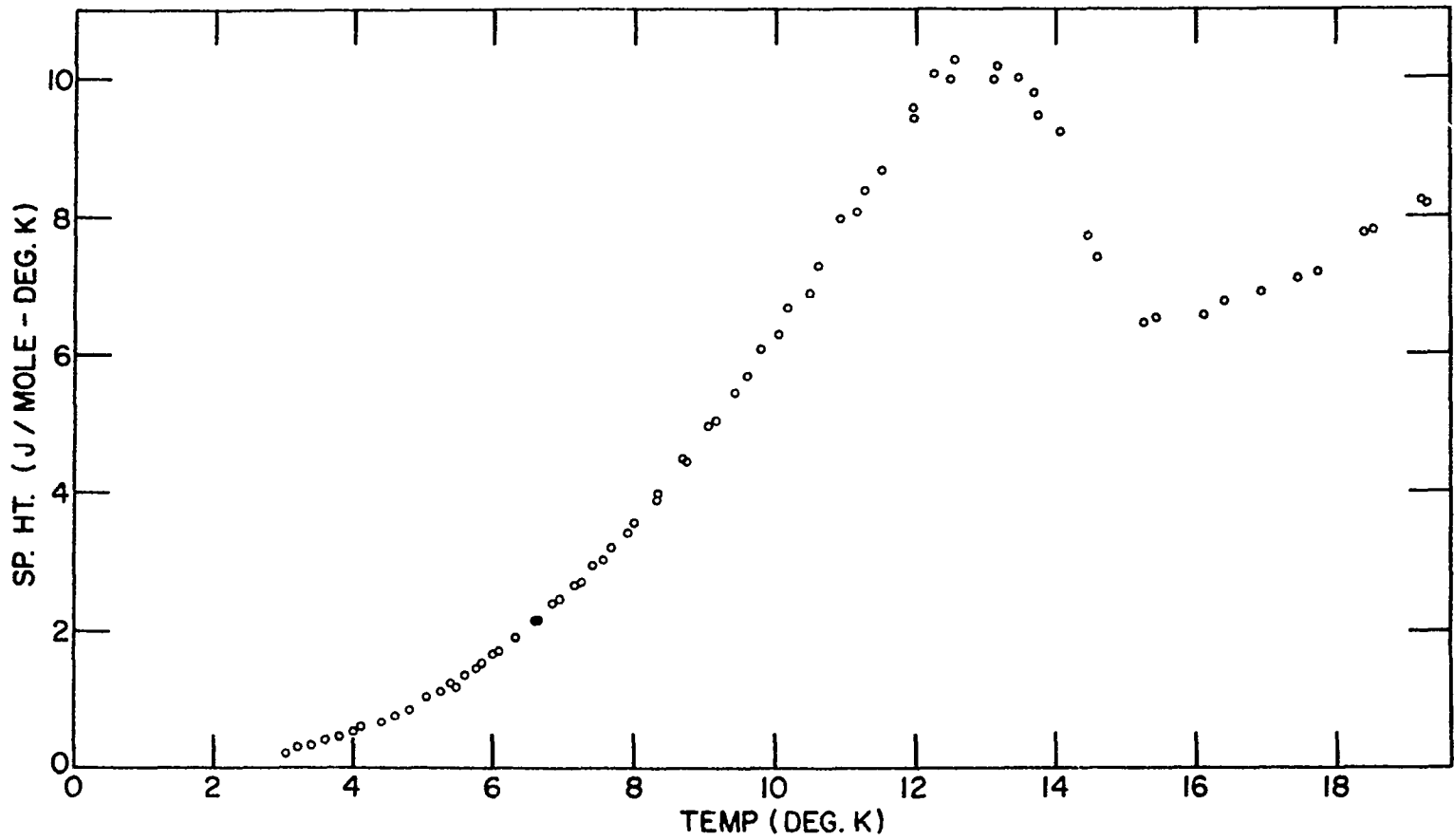


Figure 10. Specific heat vs temperature for 91%β-9%α-cerium

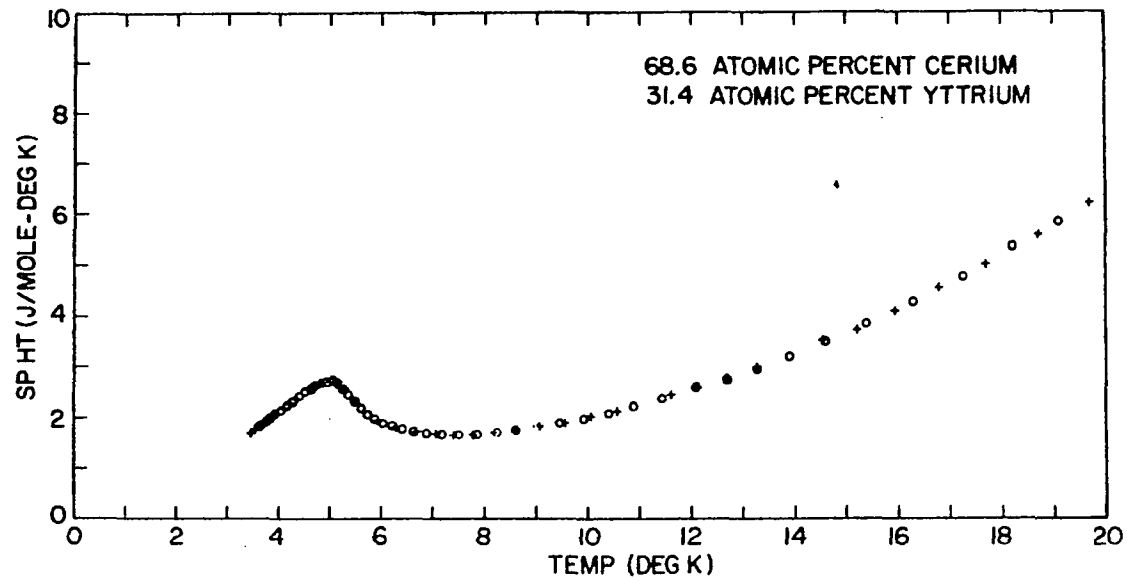


Figure 11. Specific heat vs temperature for 68.6 a/o Ce-31.4 a/o Y

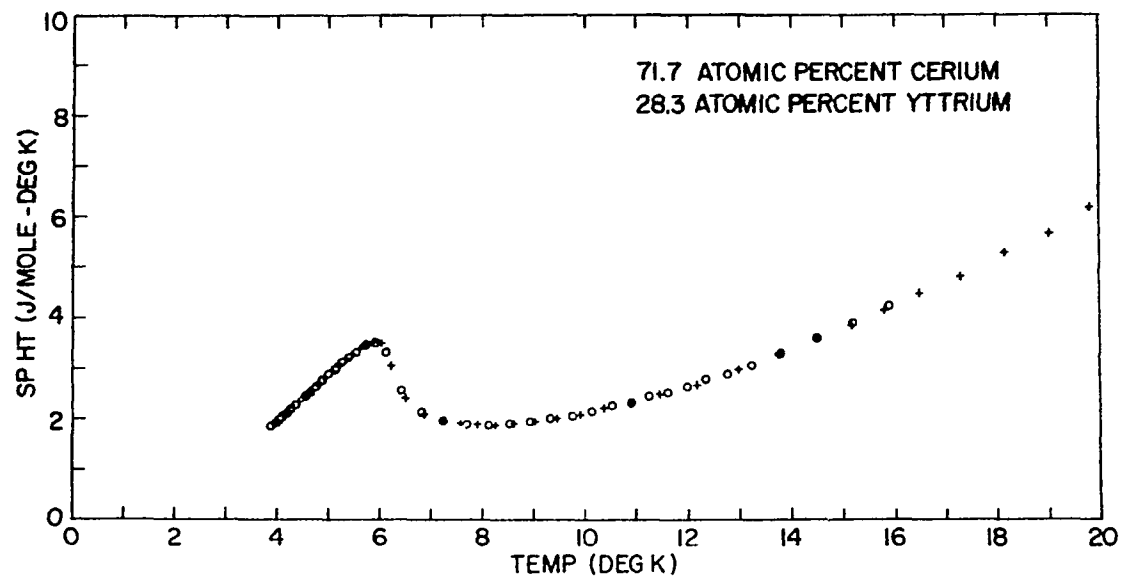


Figure 12. Specific heat vs temperature for 71.7 a/o Ce-28.3 a/o Y

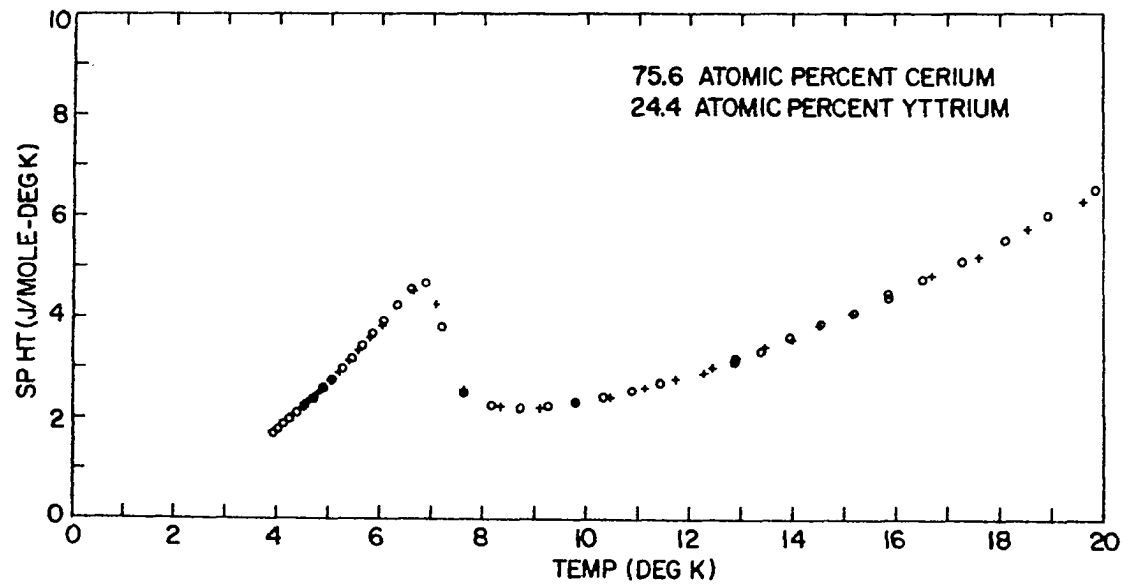


Figure 13. Specific heat vs temperature for 75.6 a/o Ce-24.4 a/o Y

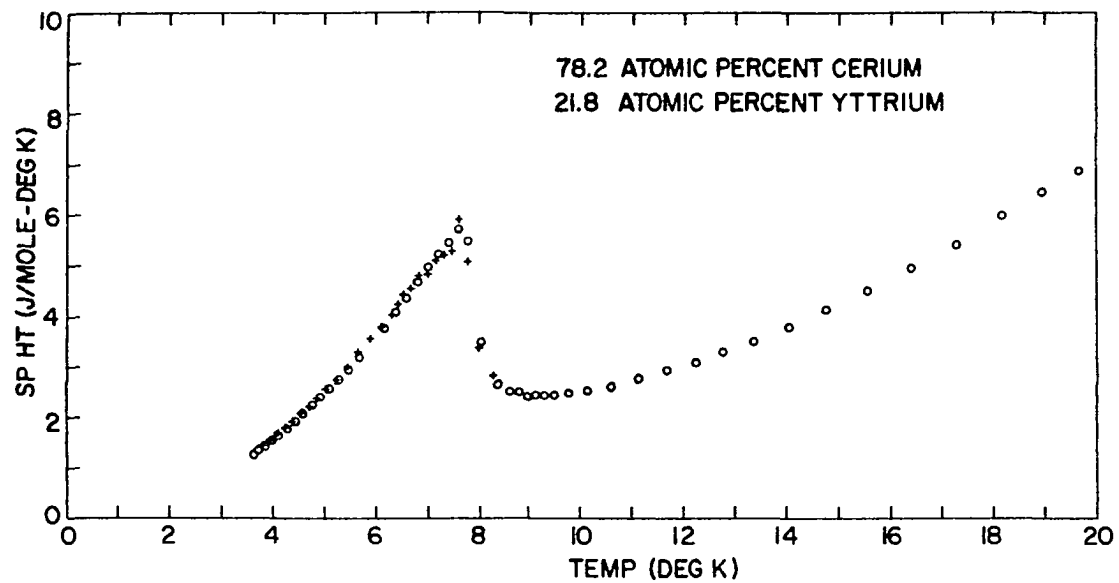


Figure 14. Specific heat vs temperature for 78.2 a/o Ce-21.8 a/o Y

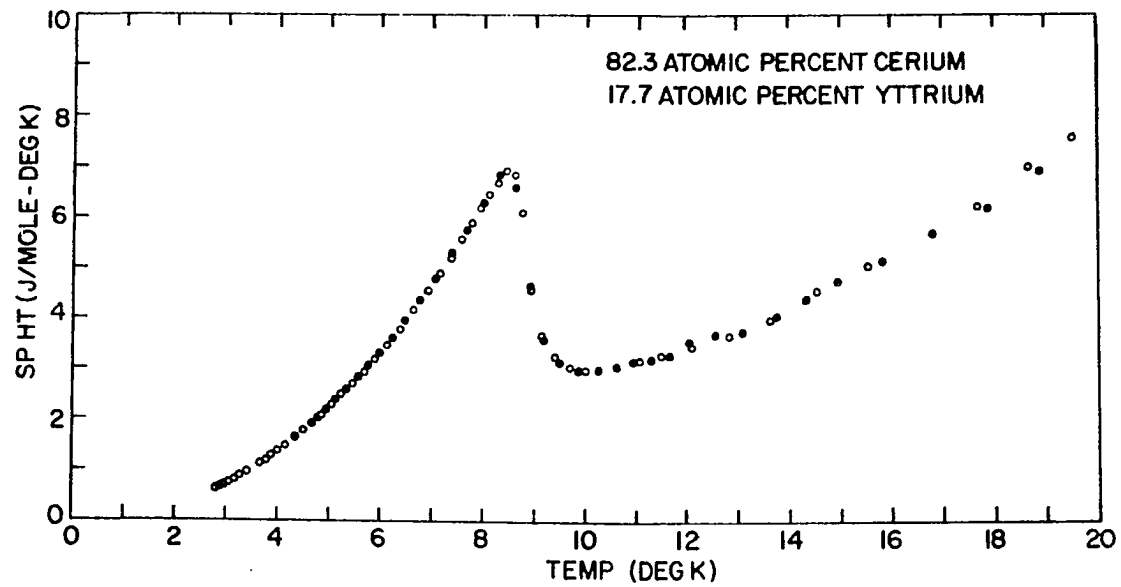


Figure 15. Specific heat vs temperature for 82.3 a/o Ce-17.7 a/o Y

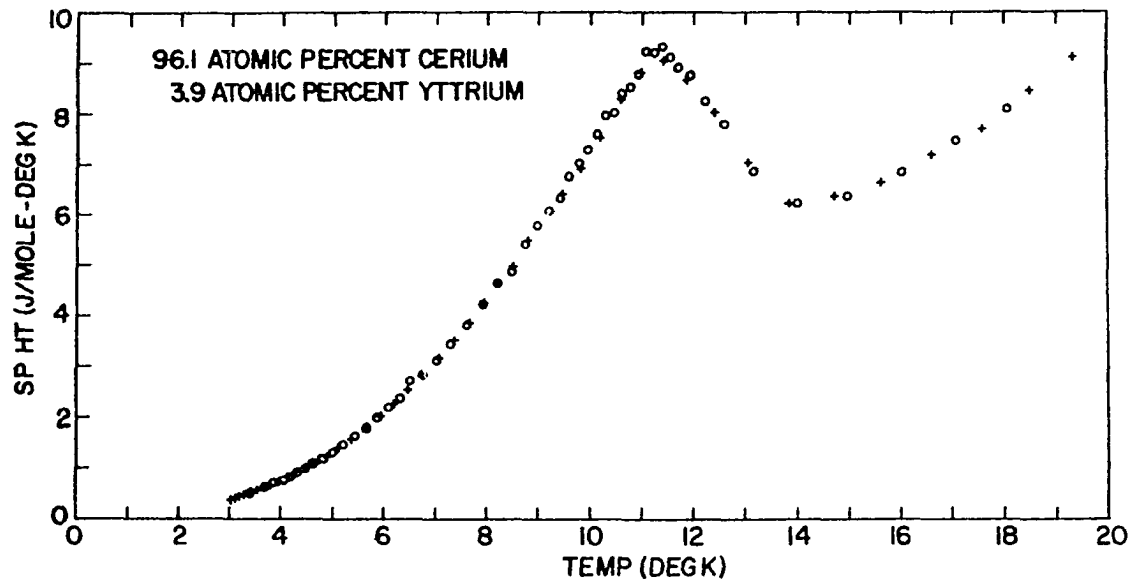


Figure 16. Specific heat vs temperature for 96.1 a/o Ce-3.9 a/o Y

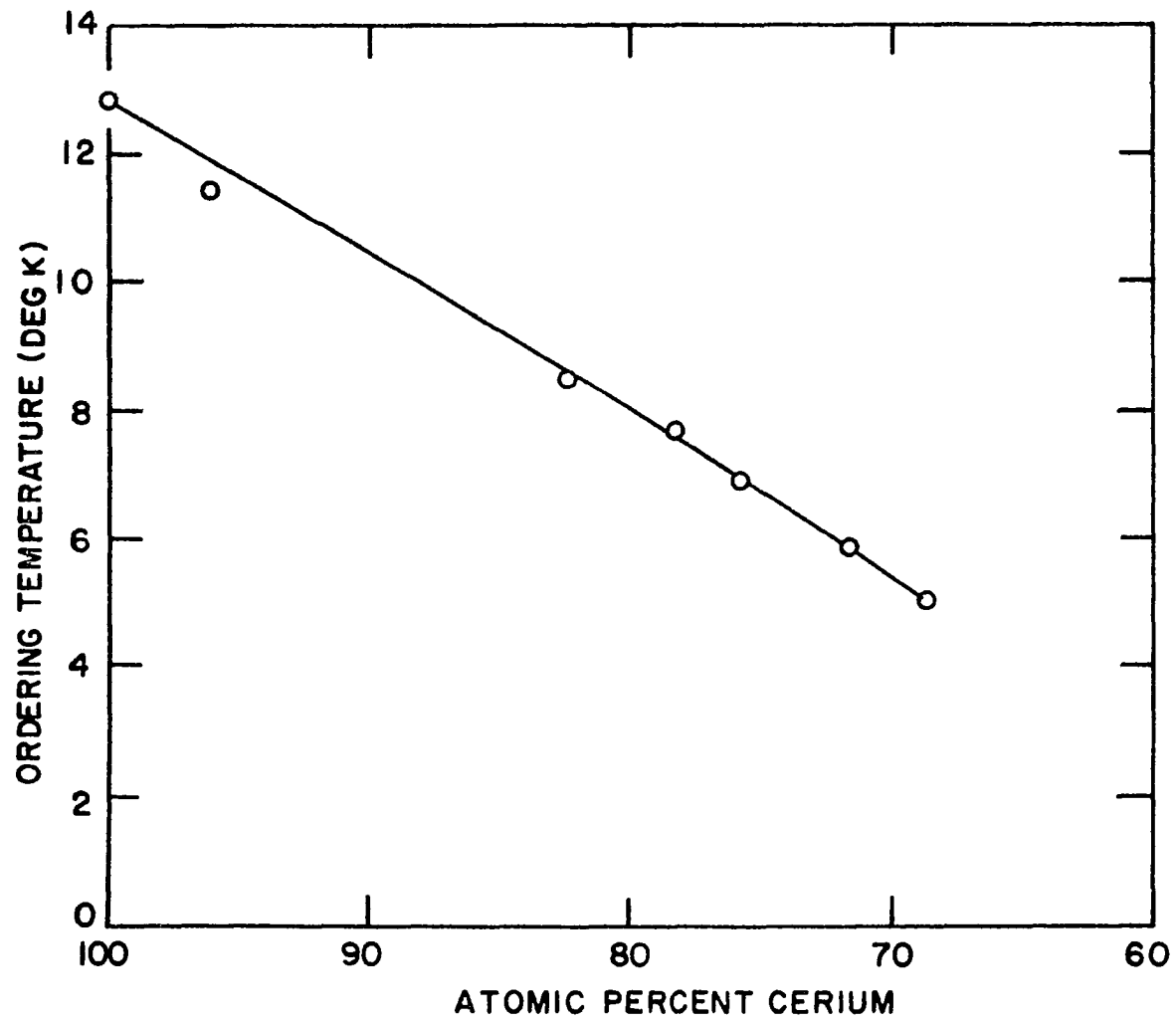


Figure 17. Ordering temperature vs atomic percent cerium

This decrease in ordering temperature with increasing yttrium content is consistent with the magnetic origin of the specific heat peaks in that the strength of the magnetic interaction is reduced by dilution and hence the ordering temperature lowered.

In contrast to the case of simple metals treated earlier the interpretation of the low temperature specific heat of magnetic systems requires a more complicated analysis. The detailed separation of the total specific heat depends on the particular system under investigation (7,8). Often the total specific heat of a magnetic system as studied here can be attributed to four terms. The first two the lattice and the electronic contributions were treated above. The third contribution is associated with the magnetic ordering of the material. The fourth contribution is due to the thermal excitation of the electrons from the ground state level to the excited higher energy levels. These excited levels arise because the crystal field around an ion removes the degeneracy of the ground state (7,8,11,29-31). In equation form:

$$C(\text{total}) = C(\text{lattice}) + C(\text{electronic}) + C(\text{magnetic ordering}) \\ + C(\text{crystal field}) \quad (9)$$

A straightforward analysis of the lattice and electronic

contributions resulting in values of γ and θ for the 91% β -9% α cerium sample and for the β -stabilized Ce-Y alloys was not possible. Essentially this was because the magnetic ordering contribution dominated the total specific heat in the low temperature region where the standard C/T vs T^2 separation is performed. Therefore values for the lattice and electronic contributions for the high β -cerium case were simply taken as equal to those of lanthanum where the results of Berman and co-workers (32) were used below the superconducting transitions and the results of Lounasmaa (33) were used for lanthanum above the transition temperatures. No correction was made to the lattice and electronic contributions to the total specific heat of the high β -cerium sample due to the presence of the 9% α -cerium. This was because the specific heats of α -cerium (measured here) and lanthanum (quoted above) are of similar magnitude and so a second order correction, estimated to be on the order of 1%, results in the total specific heat of the high β -cerium sample.

Values for the lattice and electronic contributions for the Ce-Y alloys were based on specific heat measurements made on the D.H.C.P. La-Y system by Satoh and Ohtsuke (31). These two alloy systems have the same crystal structures and the

same diluent, yttrium. Additionally, β -cerium and α -lanthanum have electronic structures which differ by one $4f$ electron. Since the measurements of Satoh and Ohtsuka were made to only 4°K it was necessary to extrapolate their results up to 23°K .

The procedure used to obtain values for the lattice and electronic contributions to the specific heat of the Ce-Y alloys was as follows. At 4°K a ratio was formed between the specific heat of a given La-Y alloy, $C(\text{La-Y}, T = 4^{\circ}\text{K})$, and the specific heat of La, $C(\text{La}, T = 4^{\circ}\text{K})$. That is, $C(\text{La-Y}, 4^{\circ}\text{K})/C(\text{La}, T = 4^{\circ}\text{K})$ was computed. At some temperature, T , between 4 and 23°K the specific heat of the alloy was obtained by multiplying the specific heat of La at that T by the above ratio. In equation form:

$$C(\text{La-Y}, T) = \frac{C(\text{La-Y}, T=4^{\circ}\text{K})}{C(\text{La}, T=4^{\circ}\text{K})} \times C(\text{La}, T) \quad (10)$$

In this manner, specific heat vs temperature curves were constructed from 4 to 23°K for the La-Y alloys measured by Satoh and Ohtsuka. Next, the specific heat was assumed to vary linearly with concentration between any two La-Y alloys so that the specific heat of an alloy of an intermediate concentration was simply obtained by linear interpolation. Finally,

the lattice and electronic contributions to the specific heat of a Ce-Y alloy measured here was taken as equal to the specific heat of the corresponding La-Y alloy as constructed above. Table 4 summarizes the γ and θ values obtained from Satoh and Ohtsuka's specific heat measurements along with those used in the present work for the Ce-Y alloys as obtained above.

Table 4. Summary of the crystal structures, γ , and θ values for the La-Y and Ce-Y alloys. Entries for the La-Y alloys were taken from Satoh and Ohtsuka (31) while those for the Ce-Y alloys were obtained as described in the text

Sample (atomic percent)	Crystal structure	γ (mj/mole- $^{\circ}$ K 2)	θ ($^{\circ}$ K)
85La-15Y	α -La	6.6	162
75La-25Y	"	6.2	170
60La-40Y	"	5.8	175
96.1Ce-3.9Y	α -Ce, β -Ce	9.8	149
82.3Ce-17.7Y	β -Ce	6.5	165
78.2Ce-21.8Y	"	6.3	168
75.6Ce-24.4Y	"	6.2	169
71.7Ce-28.3Y	"	6.1	171
68.6Ce-31.4Y	"	6.0	173

Once the lattice and electronic contributions to the total specific heat were obtained the magnetic ordering and crystal field terms could be separated. The 68.6 a/o cerium

alloy ordered at the lowest temperature, 5.05°K, and so would be the most likely to have completed its magnetic contribution by ~23°K. Therefore, somewhat arbitrarily, the total specific heat at 23°K was assumed to be the sum of the lattice, electronic, and crystal field terms. Next a smoothly decreasing curve was drawn from 23°K such that the crystal field term progressively diminished finally becoming less than 1% of the total specific heat at around 8°K, see Figure 18. The crystal field term so constructed was then assumed to be linearly dependent on the atomic percent of cerium and was used as the basis for the separation of the remaining five alloys and the β -cerium.

Valuable information can be obtained from the entropy associated with the magnetic ordering. The entropies were calculated from the equation (7,8):

$$\Delta S(\text{magnetic ordering}) = \int \frac{C(\text{magnetic ordering})}{T} dT \quad (11)$$

where $\Delta S(\text{magnetic ordering})$ = entropy associated with the
magnetic ordering

$C(\text{magnetic ordering})$ = magnetic ordering contribution
to the specific heat

T = absolute temperature

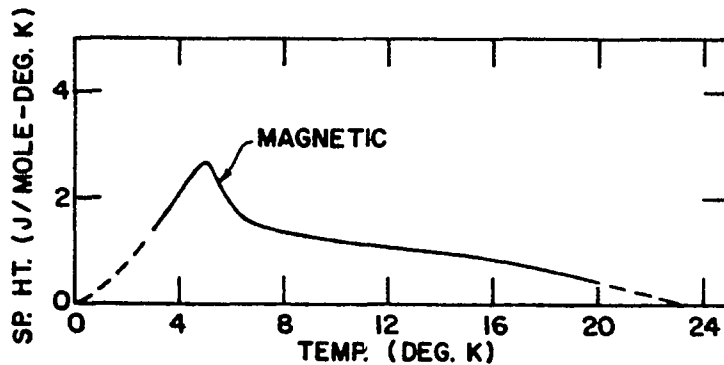
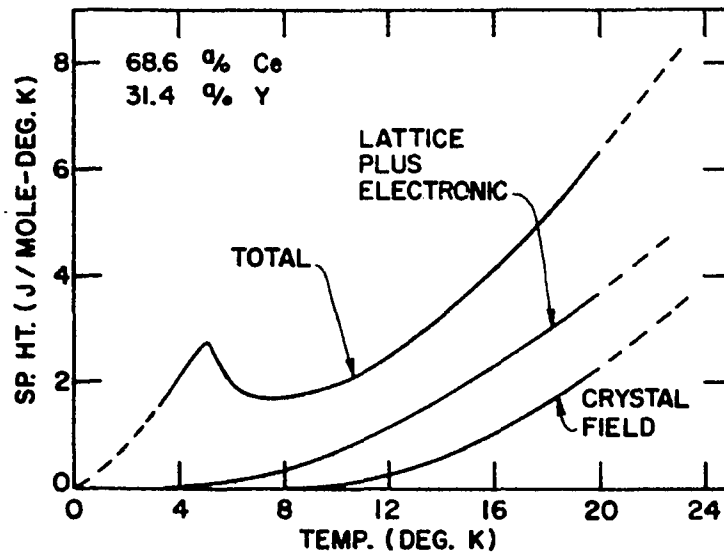


Figure 18. Separation of total specific heat of 68.6 a/o cerium alloy into (1) a lattice and electronic term, (2) a crystal field term, and (3) a magnetic term

and are summarized in Table 5.

Table 5. Summary of the measured entropies and the values of P for the high β -cerium sample and the six β -stabilized Ce-Y alloys

Alloy (a/o Ce)	Measured entropy, ΔS (j/mole- ^o K)	Values of P from $\Delta S = c R \ln P$
100	4.8 \pm .1	1.9 \pm .1
96.1	5.5 \pm .1	2.0 \pm .1
82.3	5.1 \pm .1	2.1 \pm .1
78.2	4.5 \pm .1	2.0 \pm .1
75.6	4.3 \pm .1	2.0 \pm .1
71.7	3.8 \pm .1	1.9 \pm .1
68.6	3.8 \pm .1	2.0 \pm .1

The significance of the entropy calculations stems from a result of statistical mechanics which says the entropy associated with a system of P energy levels is given by (7,8):

$$\Delta S = R \ln P \quad (12)$$

where ΔS = entropy

R = gas constant

P = number of separate energy levels

For the alloy cases, Equation 12 is modified to

$$\Delta S = c R \ln P \quad (13)$$

where

c = cerium concentration in atomic percent

Since ΔS , c, and R were known P was calculated, see Table 5.

A possible interpretation for the observed $P \simeq 2.0$ is crystal field splitting. The hexagonal crystal field surrounding the Ce^{+3} ions splits the free ion ${}^2F_{5/2}$ ground state into three doublets (30). Therefore, the ground state for the Ce^{+3} ions would be a Kramers doublet (8). The internal field associated with the magnetic ordering then splits the Kramers doublet into two levels and hence $\Delta S = c R \ln 2$.

At this point an estimate was made of the hexagonal crystal field splitting between the ground state and the two excited doublets based on the scheme used in the separation of the 68.6 atomic percent cerium alloy. From statistical mechanics the specific heat associated with these energy levels is (7,8):

$$C = \frac{Nk}{Z(kT)^2} \left\{ \sum_{r=0}^m \epsilon_r^2 g_r e^{-\frac{\epsilon_r}{kT}} - \frac{1}{Z} \left[\sum_{r=0}^m \epsilon_r g_r e^{-\frac{\epsilon_r}{kT}} \right]^2 \right\} \quad (14)$$

where C = specific heat

N = Avogadro's number

ϵ_r = energy of level r above ground state

g_r = degeneracy of level r

k = Boltzmann constant

T = absolute temperature

$$Z = \sum_{r=0}^m g_r e^{-\frac{\epsilon_r}{kT}}$$

Since N , k , m , and g_r were known the technique was to choose values for ϵ_r such that the specific heat calculated from Equation 14 fitted the experimentally observed crystal field specific heat contribution. The best fit for β -cerium was for the first and second doublets at 85 ± 5 and $110 \pm 10^\circ\text{K}$ above the ground state.

This crystal field splitting is in disagreement with Bleeney (11) who suggested the two doublets were at 30 and 150°K above the ground state. Bleeney's results are open to question on two major points. First his fit was based on specific heat measurements (12,13) which were made on multi phase cerium samples. Second since β -cerium has an atomic stacking sequence of $\cdots\text{ABACABAC}\cdots$ Bleeney assumed that one half of the Ce^{+3} ions were in a cubic crystal field while the remaining half were in a hexagonal crystal field. Nuclear magnetic resonance experiments on D.H.C.P. lanthanum (34,35) do not support this partition of D.H.C.P. into F.C.C. and simple H.C.P. A more reliable energy level scheme than either Bleeney's or the present would result from specific

heat measurements extended to higher temperatures and done on single phase samples.

Finally it was possible to consider the temperature dependence of the magnetic specific heat of the high β -cerium sample. Since this allotrope is known to order antiferromagnetically (3,5) spin wave theory predicts a cubic temperature dependence for the specific heat in a temperature region sufficiently below the Neel temperature (7,8). In equation form:

$$C(\text{antiferromagnetic}) = AT^3 \quad (15)$$

Therefore, a plot of the magnetic specific heat against the cube of the temperature should be linear. Figure 19 shows excellent agreement between theory and experiment for this sample.

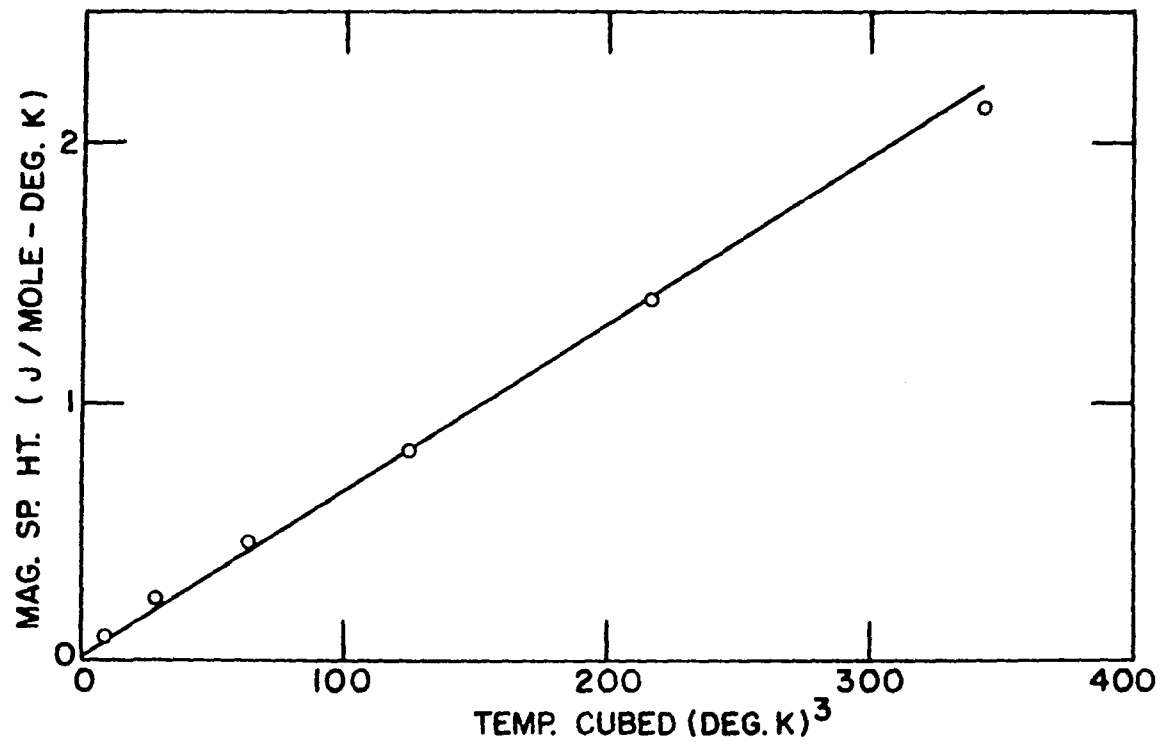


Figure 19. Magnetic specific heat of β -cerium vs temperature cubed

SUMMARY

A special technique was used to prepare pure single phase α -cerium. Its specific heat was then measured between 2.5 and 20^oK and analyzed to give an electronic specific heat constant, γ , of 9.79 ± 0.10 (mj/mole-deg K²) and a Debye temperature, θ , of 117 ± 5 ^oK. The value for θ is consistent with the observed increase in α -cerium Debye temperature with increasing pressure (23), and the value for γ is in reasonable agreement with that reported for α -cerium based on specific heat measurements done at 11 kbar pressure (22). At the lowest temperatures the standard C/T vs T² plot for α -cerium showed positive curvature. A magnetic transition in α -cerium was considered as a possible explanation for this observation.

The specific heats of 91% β -9% α -cerium and six β -stabilized Ce-Y alloys were also measured between 2.5 and 20^oK. Four principal results were obtained. First, all six alloys showed magnetic ordering characteristic of the β -cerium phase. The ordering temperature was observed to vary almost linearly with cerium concentration from 5.05^oK for the 68.6 atomic percent cerium alloy to 12.8^oK for β -cerium. This trend was consistent with the magnetic origin of the specific heat peaks. Second, the magnetic contribution to the total specific

heat for β -cerium was shown to be dependent on the third power of the absolute temperature. This was in agreement with the predicted cubic temperature dependence for an anti-ferromagnetic material based on spin wave theory (7,8).

Third, the hexagonal crystal field surrounding the Ce^{+3} ions was believed to split the free ion $^2F_{5/2}$ ground state into three doublets (30). The ground state for the Ce^{+3} ions would then be a Kramers doublet (8). The internal field associated with the magnetic ordering was then assumed to split the ground state doublet into two separate levels with an associated entropy of $R \ln 2$.

Fourth and last, the two upper doublets which resulted from the hexagonal crystal field were estimated to be 85 ± 5 and $110 \pm 10^\circ\text{K}$ above the ground state.

ACKNOWLEDGEMENTS

Many people around the Ames Laboratory have assisted me toward the completion of this thesis. With pleasure I wish to cite a few: Dr. K. A. Gschneidner, Jr., my advisor, for suggesting the problem and guiding me to its completion, Dr. R. R. Joseph for construction of an earlier calorimeter on which the present apparatus was based; M. Anderson of Dr. C. A. Swenson's Physics group for calibrating the germanium resistance thermometer which was used in the calorimeter; R. E. Hungsberg for his very able assistance in construction of the apparatus and many discussions thereafter; B. Beaudry, P. Palmer, and J. Croat of Dr. Spedding's Metallurgy group for supplying the metals used in this study; J. J. Tonnie for assistance in the low temperature dilatometry measurements; and Dr. W. A. Taylor for many helpful discussions especially concerning the interpretations of the results.

Finally I wish to thank my wife, Diana, for the numerous sacrifices she made during the period of this investigation.

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APPENDIX

MEASURED SPECIFIC HEAT OF ALPHA CERIUM

T (DEG K)	C (MJ/MOLE-K)	T (DEG K)	C (MJ/MOLE-K)	T (DEG K)	C (MJ/MOLE-K)
2.786	74.72	7.213	529.32	11.996	2173.53
3.004	91.00	7.318	544.12	12.452	2396.39
3.268	91.29	7.538	597.38	12.964	2624.04
3.538	102.32	7.734	633.17	13.430	2829.18
3.859	120.01	7.903	683.74	13.589	2925.94
4.203	143.25	8.132	730.58	14.077	3109.58
4.570	166.75	8.302	793.32	14.289	3221.17
4.769	182.90	8.537	842.40	14.703	3396.32
4.941	197.15	8.676	890.84	15.028	3541.12
5.038	206.60	9.002	988.77	15.357	3654.31
5.232	234.41	9.076	1012.10	15.819	3939.74
5.336	235.66	9.527	1157.50	16.013	4023.79
5.494	254.72	9.604	1193.08	16.611	4421.95
5.640	275.21	10.014	1327.97	16.716	4439.25
5.778	289.29	10.057	1363.37	17.438	4886.31
5.927	311.99	10.441	1530.02	17.470	4847.92
6.070	330.48	10.447	1506.48	18.170	5401.92
6.231	355.80	10.891	1696.59	18.237	5529.26
6.366	372.19	10.893	1728.62	18.292	5999.28
6.567	408.18	11.427	1909.65	18.930	6039.02
6.668	422.77	11.440	1938.82	19.471	6558.54
6.905	470.66	11.961	2149.47	19.598	6477.21
6.971	474.04				

MEASURED SPECIFIC HEAT OF 91 PERCENT BETA 9 PERCENT ALPHA CEPIUM

T (DEG K)	C (MJ/MOLE-K)	T (DEG K)	C (MJ/MOLE-K)	T (DEG K)	C (MJ/MOLE-K)
3.016	265.22	7.143	2677.29	11.950	9567.79
3.193	302.47	7.239	2719.42	11.978	9437.38
3.389	352.19	7.403	2949.69	12.262	10085.54
3.575	405.26	7.541	3031.04	12.513	9993.27
3.796	469.30	7.668	3222.62	12.561	10269.17
3.989	535.55	7.906	3436.65	13.108	9963.38
4.179	606.99	7.980	3578.96	13.152	10190.43
4.377	688.37	8.310	3900.41	13.448	10018.43
4.587	782.92	8.322	4004.81	13.712	9805.25
4.807	888.03	8.679	4500.01	13.739	9470.74
5.041	1013.10	8.729	4467.93	14.041	9233.35
5.248	1132.81	9.055	4975.81	14.447	7735.19
5.402	1246.89	9.163	5022.26	14.603	7410.68
5.483	1178.23	9.435	5483.99	15.271	6434.25
5.601	1382.46	9.604	5686.52	15.422	6522.43
5.759	1463.88	9.809	6089.72	16.129	6559.34
5.830	1543.30	10.053	6293.43	16.415	6774.72
6.044	1671.19	10.182	6689.44	16.962	6908.59
6.069	1723.84	10.495	6864.66	17.459	7108.77
6.322	1924.05	10.558	7296.09	17.766	7197.92
6.343	1911.92	10.923	7983.88	18.408	7757.53
6.590	2161.08	11.141	8062.06	18.530	7771.76
6.647	2169.51	11.278	8407.53	19.250	8221.76
6.863	2420.02	11.517	8686.44	19.329	8141.17
6.953	2455.61	11.623	7774.05		

MEASURED SPECIFIC HEAT OF 69.6 A/D CE-31.4 A/D Y

T (DEG K)	C (MJ/MOLE-K)	T (DEG K)	C (MJ/MOLE-K)	T (DEG K)	C (MJ/MOLE-K)
3.477	1688.71	5.275	2567.21	9.461	1888.37
3.554	1763.25	5.302	2567.72	9.559	1898.58
3.648	1823.65	5.383	2446.79	9.933	1974.58
3.675	1831.13	5.477	2337.41	10.067	2010.58
3.751	1912.40	5.496	2312.90	10.410	2084.18
3.754	1907.58	5.615	2186.98	10.571	2120.92
3.849	1984.09	5.691	2110.99	10.888	2216.07
3.860	2007.61	5.747	2072.45	11.450	2373.70
3.956	2072.29	5.888	1983.08	11.613	2436.54
3.978	2093.51	5.967	1936.92	12.099	2584.11
4.071	2154.44	6.040	1893.87	12.128	2582.95
4.104	2202.55	6.210	1842.99	12.690	2773.26
4.193	2252.90	6.293	1809.03	12.705	2748.83
4.231	2287.61	6.405	1776.11	13.283	2975.29
4.315	2333.11	6.628	1739.40	13.283	2944.30
4.353	2377.42	6.676	1725.40	13.907	3185.88
4.432	2419.28	6.880	1698.43	14.548	3531.09
4.543	2510.03	7.064	1679.31	14.586	3494.20
4.589	2544.35	7.182	1671.98	15.220	3721.89
4.652	2555.31	7.414	1673.47	15.393	3842.79
4.704	2605.52	7.525	1666.81	15.961	4091.59
4.758	2646.68	7.789	1676.13	16.303	4265.65
4.815	2667.84	7.860	1674.02	16.810	4545.47
4.863	2677.70	8.185	1707.36	17.269	4748.48
4.923	2695.38	8.216	1706.80	17.712	4994.66
4.966	2691.11	8.605	1740.31	18.224	5343.77
5.037	2733.98	8.615	1760.49	18.710	5560.87
5.068	2729.46	9.017	1808.33	19.097	5818.13
5.159	2692.27	9.073	1828.05	19.689	6183.12
5.171	2678.41				

MEASURED SPECIFIC HEAT OF 71.7 A/D CE-28.3 A/D Y

T (DEG K)	C (MJ/MOLE-K)	T (DEG K)	C (MJ/MOLE-K)	T (DEG K)	C (MJ/MOLE-K)
3.883	1860.66	5.485	3293.10	9.913	2093.32
3.937	1882.24	5.555	3333.35	10.148	2168.67
3.959	1917.20	5.613	3380.38	10.383	2222.75
4.022	1969.46	5.727	3463.41	10.534	2276.59
4.041	1983.35	5.737	3490.14	10.896	2334.37
4.116	2047.83	5.869	3512.36	10.897	2328.31
4.117	2050.39	5.918	3507.46	11.242	2461.70
4.194	2111.86	6.027	3498.19	11.454	2501.04
4.213	2131.35	6.132	3329.46	11.600	2537.72
4.273	2192.10	6.233	3054.18	11.976	2646.67
4.316	2215.71	6.433	2574.74	12.168	2688.43
4.358	2271.26	6.520	2415.40	12.347	2800.17
4.422	2322.51	6.828	2133.20	12.770	2904.18
4.535	2423.53	6.872	2111.85	12.985	2996.50
4.550	2447.26	7.228	1976.92	13.226	3079.54
4.655	2528.50	7.250	1972.99	13.760	3279.81
4.657	2541.61	7.574	1920.35	13.793	3305.06
4.767	2633.42	7.696	1904.74	14.488	3620.82
4.787	2659.98	7.918	1892.47	14.492	3617.90
4.862	2763.54	8.132	1885.93	15.170	3872.42
4.924	2797.08	8.258	1893.36	15.188	3915.51
5.014	2888.73	8.530	1905.87	15.805	4149.08
5.069	2938.94	8.618	1914.81	15.911	4237.69
5.142	2996.53	8.919	1950.82	16.503	4494.85
5.215	3066.06	9.007	1951.58	17.304	4825.63
5.272	3127.14	9.323	2012.25	18.155	5299.70
5.352	3178.47	9.449	2018.49	19.021	5683.24
5.410	3228.28	9.739	2068.07	19.812	6189.15

MEASURED SPECIFIC HEAT OF 75.6 A/D CE-24.4 A/D Y

T (DEG K)	C (MJ/MOLE-K)	T (DEG K)	C (MJ/MOLE-K)	T (DEG K)	C (MJ/MOLE-K)
3.943	1687.28	6.075	3806.38	12.292	2909.36
4.031	1763.38	6.091	3914.27	12.450	2969.00
4.140	1868.66	6.344	4206.75	12.895	3131.37
4.263	1964.38	6.623	4541.05	12.900	3170.62
4.401	2093.04	6.664	4524.37	13.397	3306.08
4.538	2175.70	6.899	4657.66	13.473	3382.27
4.561	2234.87	7.076	4233.31	13.959	3579.94
4.564	2241.16	7.202	3807.03	14.002	3536.40
4.623	2291.12	7.630	2516.70	14.534	3824.70
4.709	2358.03	7.644	2484.89	14.562	3863.23
4.733	2379.46	8.173	2228.28	14.151	4054.73
4.805	2466.13	8.341	2210.97	15.198	4084.20
4.907	2573.27	8.705	2176.73	15.870	4447.34
4.919	2576.12	9.093	2180.40	15.877	4368.29
5.056	2721.32	9.249	2215.78	16.540	4743.29
5.083	2745.78	9.794	2282.43	16.714	4799.04
5.220	2903.27	9.784	2295.59	17.288	5081.58
5.280	2963.24	10.335	2393.76	17.613	5174.99
5.407	3108.08	10.467	2390.77	18.105	5502.02
5.482	3182.71	10.895	2527.38	18.562	5722.46
5.610	3314.51	11.136	2568.57	18.943	5988.30
5.678	3418.15	11.433	2681.95	19.624	6258.92
5.827	3589.34	11.736	2758.54	19.850	6491.05
5.879	3645.32				

MEASURED SPECIFIC HEAT OF 78.2 A/O CE-21.8 A/O Y

T (DEG K)	C (MJ/MOLE-K)	T (DEG K)	C (MJ/MOLE-K)	T (DEG K)	C (MJ/MOLE-K)
3.625	1265.54	5.677	3203.41	8.256	2824.19
3.721	1342.35	5.897	3562.13	8.356	2655.71
3.809	1433.84	6.120	3797.02	8.629	2520.63
3.839	1434.13	6.146	3776.18	8.819	2496.77
3.952	1538.55	6.298	4039.78	8.980	2409.22
3.971	1542.07	6.378	4082.01	9.135	2438.32
4.097	1689.04	6.434	4236.21	9.301	2442.85
4.113	1657.74	6.548	4420.60	9.504	2443.35
4.248	1811.76	6.600	4355.28	9.781	2480.46
4.269	1789.09	6.682	4543.36	10.165	2529.25
4.399	1927.98	6.808	4667.71	10.620	2613.85
4.431	1923.17	6.834	4804.80	11.124	2754.37
4.552	2076.35	6.997	4826.85	11.670	2917.32
4.595	2074.16	7.011	4961.38	12.236	3077.66
4.706	2212.43	7.158	5087.94	12.762	3299.91
4.760	2235.75	7.208	5224.56	13.358	3504.50
4.862	2392.68	7.319	5190.41	14.041	3784.08
4.929	2396.53	7.399	5438.40	14.764	4138.82
5.027	2556.23	7.475	5274.88	15.551	4499.30
5.101	2572.63	7.586	5712.84	16.398	4954.06
5.224	2743.85	7.621	5895.38	17.290	5405.03
5.275	2746.89	7.780	5473.56	18.166	5992.21
5.438	2984.77	7.785	5076.97	18.957	6461.06
5.464	2952.11	7.994	3380.68	19.655	6874.81
5.656	3284.30	8.026	3486.22		

MEASURED SPECIFIC HEAT OF 82.3 A/O CE-17.7 A/O Y

T (DEG K)	C (MJ/MOLE-K)	T (DEG K)	C (MJ/MOLE-K)	T (DEG K)	C (MJ/MOLE-K)
2.829	628.65	6.009	3269.42	9.680	2992.23
2.894	662.32	6.147	3436.48	9.881	2949.12
2.976	701.51	6.249	3586.98	9.964	2939.24
3.073	752.23	6.416	3764.59	10.249	2958.22
3.181	811.95	6.514	3918.35	10.259	2962.83
3.296	878.57	6.683	4142.20	10.604	3006.42
3.418	951.61	6.797	4321.91	10.621	2975.06
3.674	1115.93	6.934	4503.03	10.937	3106.09
3.786	1189.07	7.093	4745.25	11.038	3124.63
3.893	1261.88	7.168	4841.83	11.300	3153.36
4.023	1363.85	7.383	5191.33	11.533	3238.55
4.169	1472.24	7.391	5252.05	11.683	3239.38
4.331	1600.94	7.586	5534.49	12.086	3483.45
4.361	1626.24	7.701	5716.15	12.119	3410.35
4.506	1746.41	7.779	5840.98	12.586	3640.51
4.520	1749.51	7.961	6146.14	12.836	3635.70
4.669	1884.29	8.010	6243.51	13.113	3700.29
4.689	1903.79	8.136	6424.51	13.647	3949.23
4.807	2004.84	8.302	6669.03	13.761	4008.66
4.878	2040.81	8.320	6817.42	14.357	4353.95
4.972	2160.24	8.460	6895.01	14.554	4503.61
5.076	2262.42	8.619	6811.45	14.970	4713.58
5.163	2345.92	8.652	6565.39	15.539	5007.32
5.279	2463.18	8.769	6053.85	15.822	5089.78
5.369	2558.50	8.928	4586.25	16.813	5630.94
5.490	2686.44	8.934	4528.14	17.689	6138.37
5.589	2804.09	9.154	3593.85	17.862	6146.59
5.697	2903.01	9.187	3539.01	18.673	6933.43
5.798	3030.45	9.408	3193.11	18.899	6887.32
5.907	3155.45	9.512	3091.65	19.521	7533.13

MEASURED SPECIFIC HEAT OF 96.1 A/D CE-3.9 A/D Y

T (DEG K)	C (MJ/MOLE-K)	T (DEG K)	C (MJ/MOLE-K)	T (DEG K)	C (MJ/MOLE-K)
3.036	394.23	5.926	2040.42	10.304	7958.11
3.105	411.33	6.095	2188.05	10.475	8006.12
3.193	439.49	6.198	2271.81	10.596	8280.12
3.303	475.88	6.318	2384.02	10.635	8409.67
3.398	508.68	6.466	2535.53	10.798	8528.87
3.422	516.63	6.523	2722.58	10.951	8789.92
3.544	564.20	6.755	2823.16	11.004	8808.03
3.678	614.25	6.757	2842.58	11.095	9218.70
3.698	621.78	7.024	3118.49	11.246	9215.73
3.820	674.21	7.067	3170.19	11.396	9323.17
3.884	697.35	7.314	3450.55	11.419	9052.98
3.974	740.96	7.381	3520.72	11.560	9111.50
4.038	769.12	7.623	3821.65	11.739	8916.39
4.038	769.12	7.674	3861.26	11.880	8659.65
4.140	822.95	7.930	4229.84	11.961	8773.79
4.183	844.98	7.951	4268.15	12.231	8246.74
4.301	901.03	8.223	4644.65	12.411	8032.71
4.324	917.64	8.227	4644.26	12.604	7790.56
4.467	993.14	8.505	4880.43	13.065	7028.94
4.471	992.28	8.507	4965.17	13.168	6870.64
4.630	1089.30	8.758	5416.15	13.845	6236.49
4.662	1106.99	8.799	5495.85	13.980	6233.41
4.809	1194.61	8.994	5782.69	14.708	6363.08
4.879	1242.37	9.218	6081.77	14.962	6370.14
5.005	1324.01	9.429	6330.32	15.619	6643.57
5.113	1398.51	9.472	6409.29	16.019	6849.20
5.214	1471.71	9.601	6768.40	16.596	7196.16
5.366	1582.89	9.778	7022.33	17.079	7472.98
5.430	1626.82	9.818	6896.79	17.586	7685.55
5.636	1794.67	9.958	7285.56	18.082	8095.07
5.650	1800.45	10.136	7591.80	18.514	8469.99
5.874	1989.31	10.196	7520.51	19.345	9107.92