

Heat capacity measurements from 150 mK to 1.5 K  
on some  $\text{CeSi}_x$  metallic alloys

by

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A Thesis Submitted to the  
Graduate Faculty in Partial Fulfillment of the  
Requirements for the Degree of  
MASTER OF SCIENCE

Department: Materials Science and Engineering  
Major: Metallurgy

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Signatures have been redacted for privacy

Iowa State University  
Ames, Iowa

1987

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## I. INTRODUCTION

Heat capacity measurements consist of measuring the temperature response of a thermally isolated material to a known amount of heat. The specific heat of the material can be calculated if the mass and formula weight are known. Since it is not possible to completely thermally isolate a sample (due to external heat leaks) the measurement of heat capacity involves the use of semi-adiabatic methods to obtain data.

The measured heat capacity of a material gives insight into the distribution of energy levels associated with that material. The electronic, lattice, and magnetic contribution to the heat capacity can be determined by fitting the experimental data to various models. A review of low temperature heat capacity of metals and discussion on the various contributions to heat capacity data can be found in references 1 and 2.

### A. Low Temperature Heat Capacity Measurements

Low temperature calorimeters were first developed in the early 1900's by Nernst,<sup>3</sup> and Eucken.<sup>4</sup> Through the years, calorimetry techniques have become more precise with the development of accurate thermometers and electronic equipment.

Heat capacity measurements in the temperature range 1.5 K-30 K have been done on a variety of materials using many

different techniques.<sup>5</sup> These techniques can be modified so that the temperature range can be extended upwards towards higher temperatures. Extending the temperature range downward becomes more difficult.

The problem with measuring heat capacity at low temperatures is that most materials have exceedingly small heat capacities. Making the measurement more difficult are small sample sizes. New materials are usually not available in large quantities. In addition, nonadiabatic conditions resulting from heat leaks into a low temperature system can make the data analysis more complicated.

In order to obtain accurate data at low temperatures, the sample holder, thermometer, and sample heater (collectively referred to as the addenda) must have a smaller heat capacity than that of the sample being measured. The addenda heat capacity is subtracted from the total measured heat capacity in order to determine the sample heat capacity.

The other requirement for low temperature heat capacity measurements is a method for cooling the sample. A widely used method is dilution refrigeration. This method of cooling is achieved by circulating dilute amounts of liquid  $^3\text{He}$  through liquid  $^4\text{He}$ .<sup>6</sup> The commercial development of dilution refrigerators has provided a convenient method of cooling materials below 1 K. Other methods of cooling are discussed in reference 7.

## B. $\text{CeSi}_x$ Metallic Alloys

The metallic alloys in the series  $\text{CeSi}_x$  ( $1.60 \leq x \leq 2.00$ ) have been previously studied to understand the various low temperature states.<sup>8</sup> The alloys have been found to behave as valence fluctuation compounds or as ferromagnetic dense Kondo systems depending upon the concentration of silicon.

$\text{CeSi}_2$  and the Si deficient alloys  $\text{CeSi}_x$  ( $x > 1.85$ ), are considered intermediate valence fluctuation compounds.<sup>9</sup> As the silicon concentration is further decreased, the alloys order ferromagnetically. For compositions  $\text{CeSi}_x$  ( $1.55 < x < 1.85$ ), the system is considered a ferromagnetically ordered dense Kondo system.<sup>10,11</sup> The sublattice of Ce atoms orders via the Ruderman, Kittel, Kasuya, and Yosida (RKKY) interaction while the reduction in the observed magnetic moment is explained by the Kondo effect. For a discussion of the Kondo effect and RKKY interactions in metals see reference 1.

Recent measurements of heat capacity, ac susceptibility, and resistivity have indicated that the onset of magnetic ordering occurs at  $\text{CeSi}_x$  ( $x = 1.85$ ).<sup>12</sup> The alloys  $\text{CeSi}_{1.820}$  and  $\text{CeSi}_{1.830}$  order ferromagnetically at 8.4 K and 5.5 K respectively.  $\text{CeSi}_{1.850}$  appears to order at approximately 1 K as determined by low field ac susceptibility measurements.

In this study, the calorimeter will be used to examine the contributions to the heat capacity in the region of the magnetic to nonmagnetic transition in  $\text{CeSi}_x$  system.

## II. CALORIMETER DESIGN

The calorimeter design used for these measurements is based on a combination of designs found in the literature.<sup>13,14,15</sup> It is designed to be bolted to the mixing chamber of a commercial dilution refrigerator.<sup>16</sup> A removable addenda holder allows samples to be changed without removing the bellows heat switch assembly. A thermal shield encloses the addenda support. All components are made of type 101 copper and are gold plated to prevent oxide formation. The gold plating procedure is described in Appendix A. Other plating solutions can be found in Rosebury.<sup>17</sup> The mounting flange, addenda holder, thermal shield, and addenda are shown in Figures 1, 2, and 3. A description of the design details are below.

### A. Addenda

The addenda consists of two sapphire substrates that are bolted together. One substrate has a unencapsulated germanium resistance thermometer varnished to one side while the other substrate has a strain gauge varnished to one of its sides. General Electric 7031 varnish is used to hold the components in place. The 350 ohm strain gauge<sup>18</sup> is used as a sample heater. An evaporated gold heater had been tried initially but the delicate nature and poor adhesion of the film prevented its use. The samples are held in place by bolting the two

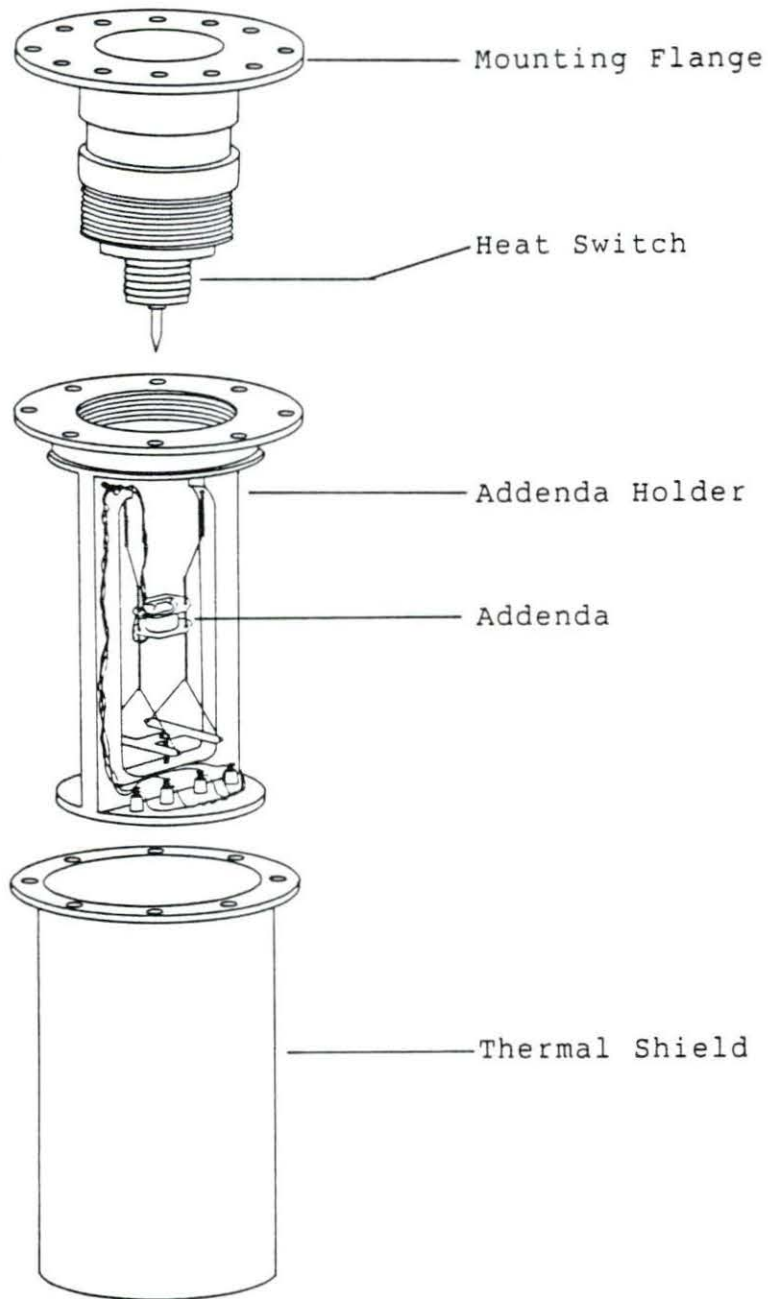


Figure 1. Calorimeter for use on a dilution refrigerator



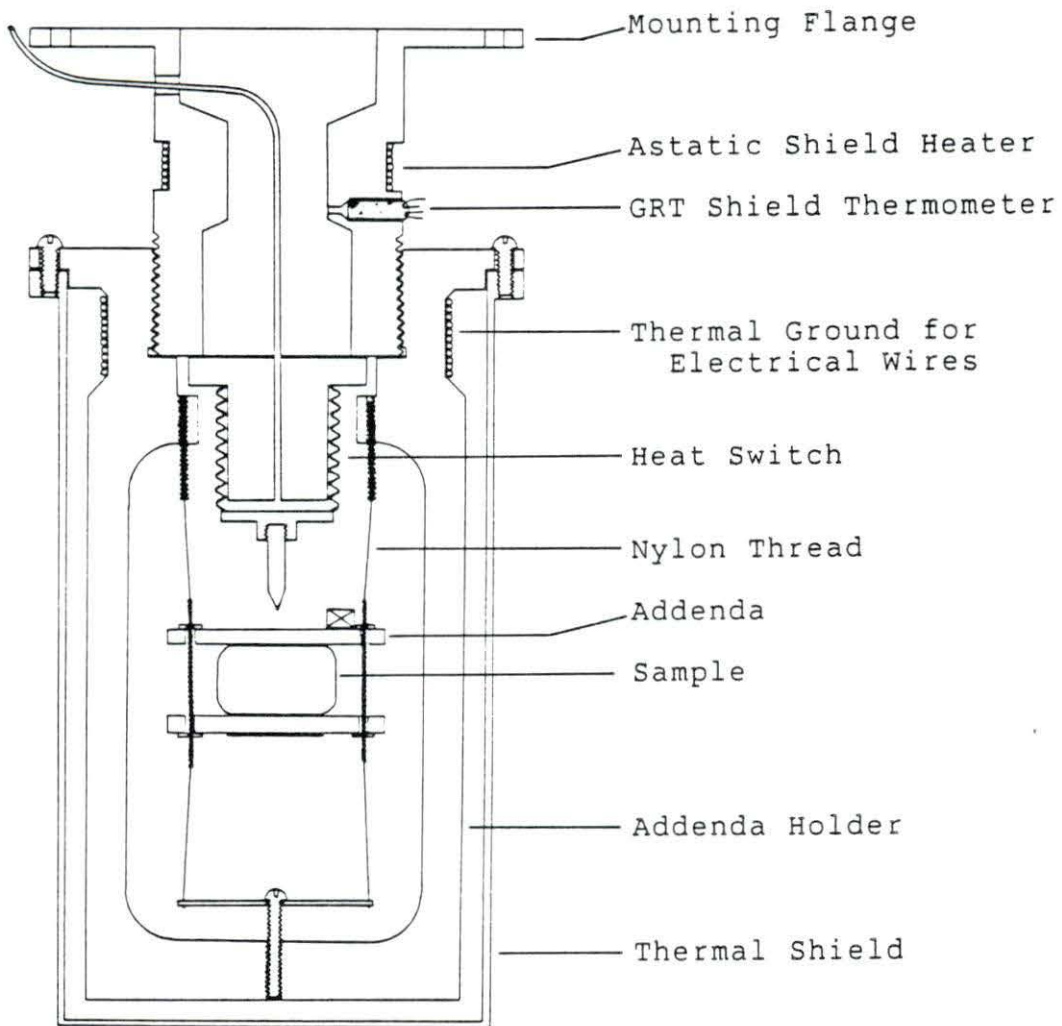


Figure 2. Cross sectional view of calorimeter

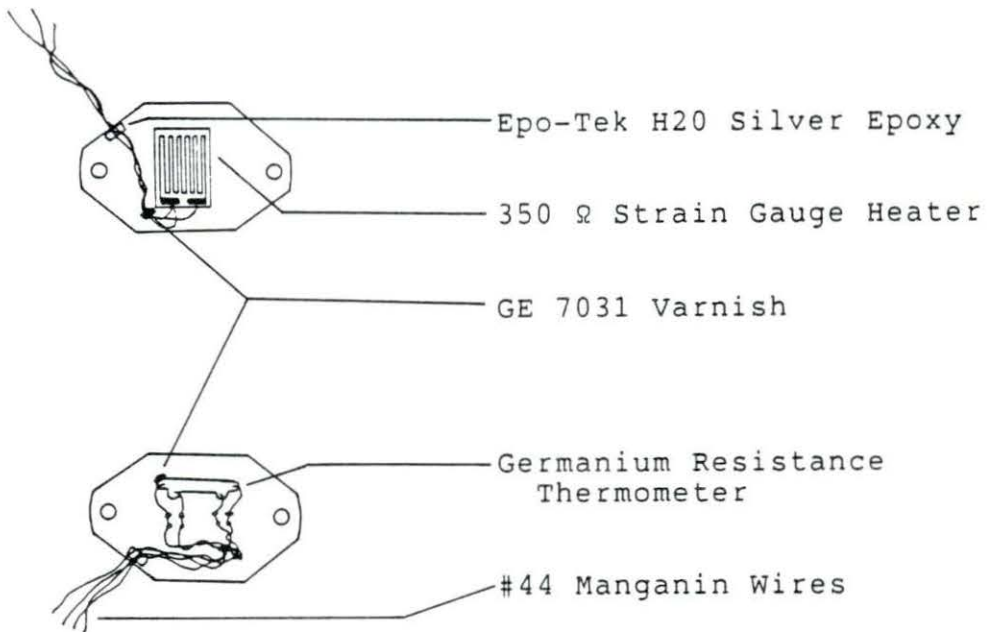
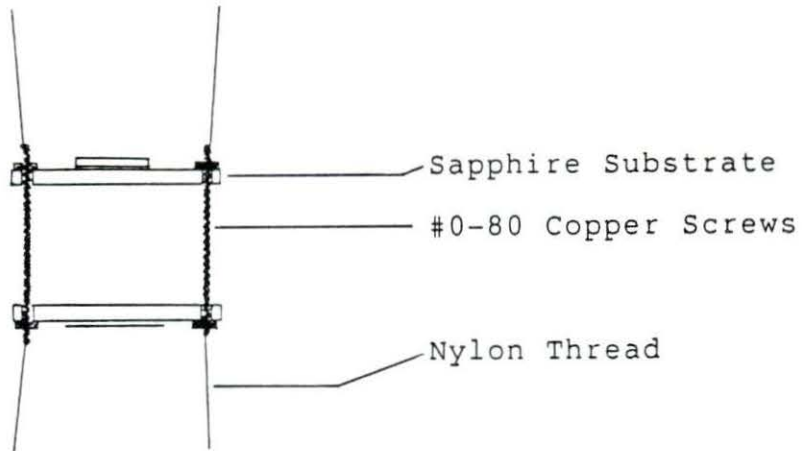


Figure 3. Addenda side view, heater substrate, and thermometer substrate

substrates together with #0-80 copper screws. The copper screws were fabricated by threading a piece of #16 gauge work hardened copper wire. Nylon screws were used initially but proved unsuccessful due to the poor thermal conductivity of nylon. In addition to the clamping force provided by the copper screws, the faces in contact with the sample are rough ground (to increase the surface area) and have a small amount of Apiezon M grease on them. The grease provides additional thermal contact between the sample and addenda. All electrical connections to the addenda (4 wires for the thermometer and 3 wires for the heater) are made with #44 manganin wire. The leads are approximately 10 cm long. The thermometer has two twisted pairs silver epoxied and varnished to the substrate with the actual contact to the gold thermometer leads made with silver print. The heater uses a twisted triplet with the wires epoxied and varnished to the substrate and soldered to the strain gauge. One voltage lead is connected to the heater on the addenda while the other voltage lead is connected at the addenda holder. This method compensates for the heat being generated in the current leads. Figure 3 shows the addenda assembly. The addenda is supported in the holder by 0.125 mm diameter nylon thread. Several methods of supporting the addenda were tried in order to eliminate problems with vibrational heating. The addenda was finally suspended from the addenda holder using a 6 point suspension (see Figure 1).

## B. Heat Switch

The heat switch provides a means of cooling the addenda and sample to the lowest possible temperature. Since the switch is a mechanical type contact, vibrational heating is observed when the sample is isolated. However, after isolation the sample temperature drifts down towards the minimum temperature of the dilution refrigerator. The heat switch is shown in Figure 4. A Be-Cu bellows is pressurized with  $^4\text{He}$  gas in order to extend the bellows and make contact to the addenda. The gas volume is kept small to limit the heating of the mixing chamber when the gas is introduced and to limit the volume of condensed liquid. As the liquid condenses, an equilibrium is reached and a gas/liquid interface is established in the pressurizing capillary. Maintaining pressure on the interface keeps the bellows extended. In order to isolate the sample, the volume of liquid is pumped. The restoring force of the bellows breaks the contact thereby thermally isolating the sample. Approximately 1-2 atmospheres of  $^4\text{He}$  gas pressure are sufficient to expand the bellows 2-3 mm.

## C. Thermal Shield

A seamless copper thermal shield encloses the sample and the addenda. The shield temperature is adjusted in order to maintain a temperature similar to that of the sample. A

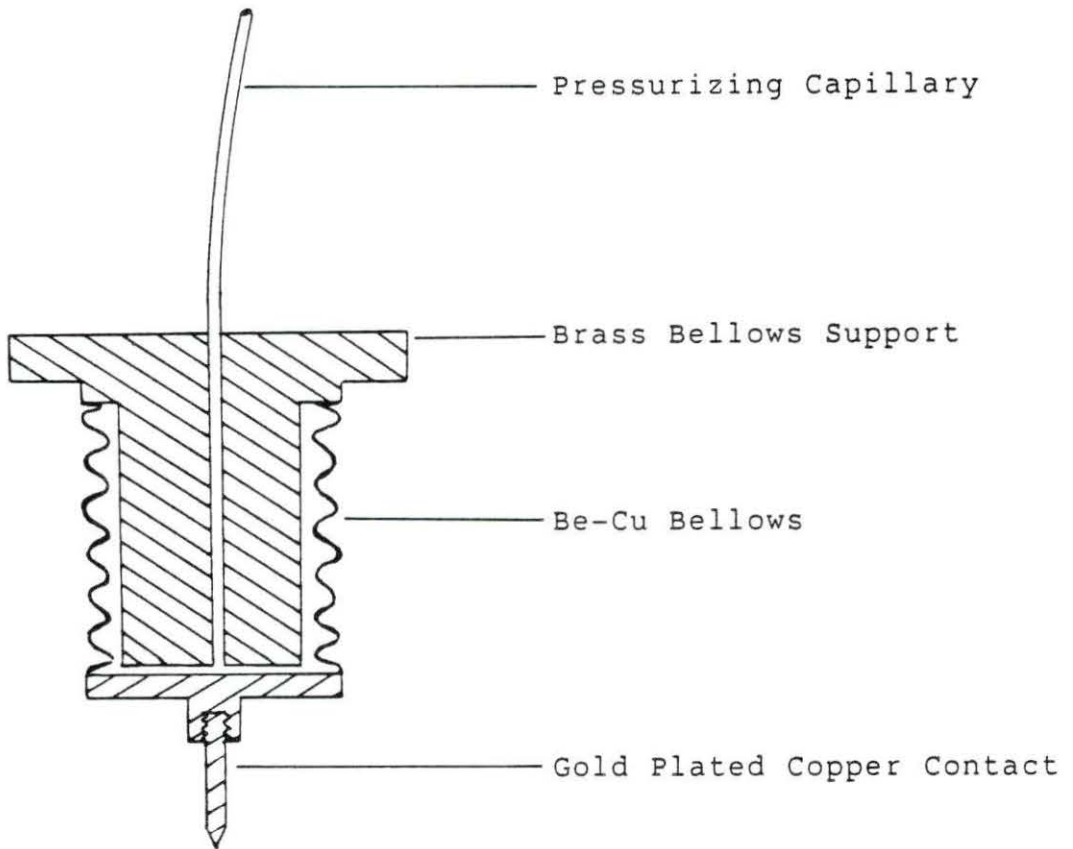


Figure 4. Cross sectional view of bellows heat switch

germanium resistance thermometer is used to monitor the shield temperature. A temperature controller supplies current to a 500 ohm astatic shield heater in order to maintain the desired temperature. The shield heater is wound and varnished on the mounting flange (see Figure 2). The thermal shield bolts to the addenda holder. A small amount of Apiezon M grease is used between the mating flanges to insure good thermal contact.

### III. EXPERIMENTAL METHODS

The calorimeter is designed to operate as a semi-adiabatic device. The method of data acquisition utilizes a standard heat pulse technique. The thermometer used for the temperature measurement is a germanium resistance thermometer. A description of the thermometer calibration, cool down procedure, and data analysis follows.

#### A. Thermometer Calibration

An uncalibrated, unencapsulated germanium resistance thermometer with approximately 42 ohms resistance at 4.2 K was obtained from Cryocal.<sup>19</sup> The thermometer was calibrated against a standard calibrated germanium resistance (NBS traceable) down to 0.3 K and against a cerium magnesium nitrate (CMN) thermometer from 0.3 K to 60 mK. The CMN thermometer was calibrated against the calibrated germanium thermometer in the temperature range above 0.3 K. The uncalibrated thermometer was varnished by one end (in order to avoid strains) to a copper block along with the calibrated thermometer. The copper block was then bolted to the mixing chamber of the dilution refrigerator in close proximity to the CMN thermometer. The conductance of the uncalibrated thermometer was measured at temperatures determined by the calibrated thermometer to obtain a plot of resistance versus temperature. The data were scaled using the relation

$$\ln(R) = Ax+B$$

with A and B chosen such that  $-1 \leq x \leq 1$ . The data were least squares fit in the temperature range 0.6 K to 1.5 K to the equation of the form

$$\ln(T) = \sum_{i=1}^N A_i x^i$$

The fit resulted in a root mean square deviation of 0.447 mK for a polynomial of degree 13. The coefficients were entered into a HP-97 calculator for use in the heat capacity program. For the temperature range above 1.5 K another fit was made to obtain a calibration. Further discussion on thermometer calibration and temperature scales can be found in references 7, 20, and 21.

#### B. Sample Cooling and Measurement

Prior to measurement, the sample was weighed to accurately determine the mass. Since Apiezon M grease was used for thermal contact between the addenda and sample, careful accounting of mass changes was necessary to ensure that the amount of grease subtracted and added to the addenda did not change. When the samples were removed after measurement, the increase in mass was noted and the next sample received some grease if needed. Usually mass increases were less than 1 mg. The addition of grease was necessary in order to prevent the addenda heat capacity from changing.



The samples were mounted in the addenda and the tension on the nylon threads was adjusted via the lower suspension assembly (see Figure 1). After the addenda holder was threaded onto the mounting flange, the heat switch was adjusted so that the point contact was ~2-3 mm away from the sapphire substrate. The electrical contacts were made and checked for continuity. After the final checkout, the radiation/thermal shields were put in place and the calorimeter and refrigerator were sealed in a vacuum can.

The refrigerator was cooled to liquid helium temperatures by one of two methods. The first method involved transferring liquid nitrogen into the superinsulated dewar (with 2 Torr nitrogen exchange gas in the vacuum can) and then waiting for the system to cool to ~80 K before transferring out the liquid nitrogen. After the nitrogen is pumped out of both the dewar and vacuum can, liquid helium could be transferred into the dewar (with 200 mTorr helium exchange gas in the vacuum can). This method usually required one day to cool from room temperature to 4.2 K. The second method is a much faster procedure for cooling to liquid helium temperatures. This method requires more liquid helium since the liquid nitrogen transfer is eliminated and cool down from room temperature to 4.2 K is accomplished with cold  $^4\text{He}$  gas. The key to this method is a slow transfer. Cold  $^4\text{He}$  gas cools just as effectively as liquid  $^4\text{He}$ . A transfer of 2-3 hours (instead of one hour when cooling down from 80 K) only requires an

additional 5-7 liters of liquid  $^4\text{He}$  than with the previous method. The advantage of the second method is that the possibility of clogging the coldplate capillary inlet (which is essential for the refrigerator to operate) is minimized and the entire cool down can be accomplished in several hours instead of one day. Usually the second method was used if the dilution refrigerator was just warmed up and the dewar was still cold. It was possible to warm up the dilution refrigerator from 1 K to room temperature, change calorimeter samples, and cool back down to 1 K in less than 18 hours using the second method.

Following the cool down to 4.2 K, the dilution refrigerator required a bake-out to help pump out the helium exchange gas that had been used during the cool down. The helium gas must be completely removed in order to thermally isolate the dilution refrigerator from the liquid helium bath and also to eliminate the problem of helium gas deabsorbing from the sample during heat capacity measurements. Deabsorption of helium gas from the sample during the heat pulse gives rise to additional heat capacity. In order to eliminate the problems associated with helium, a cool down with no exchange gas in the vacuum can was tried. It was found that the refrigerator was too well isolated to cool to 4.2 K in a reasonable length of time.

The dilution refrigerator was typically operated for about 12 hours before the sample was at minimum temperature. When the heat switch was used, vibrational heating was observed when

the point contact touched the substrate. It was found that most samples would cool to the lowest temperatures without the heat switch if the refrigerator was allowed to operate for a longer period of time (thermal conduction through the electrical leads and radiation from the thermal shield were sufficient to cool most samples).

With the sample at the lowest temperature and isolated, the heat capacity was measured. The shield heater and mixing chamber heaters were adjusted to slowly warm the sample and refrigerator. As the temperature was increased, measurements were made. Care was taken to ensure that the shield temperature was approximately the same as the sample in order to prevent drifts in the sample temperature. Instabilities in the refrigerator made it difficult to take data above 1.3 K. Most of the  $^3\text{He}/^4\text{He}$  gas in the refrigerator needed to be pumped out in order to get data between 1.3 K and 2.1 K. Measurements above 2.1 K were not possible.

### C. Data Analysis

Data were obtained using a standard heat pulse technique. A known amount of heat was applied to the sample and its temperature response was measured to determine the heat capacity. An operational amplifier constant current source was used to provide current to the strain gauge sample heater. Further details concerning the current source and other

electronics can be found in reference 22. The power applied to the heater was determined by measuring the voltage drop across a standard resistor ( $R_S=347.36\Omega$ ), the voltage drop across the heater, and the duration of the heat pulse. The constant current was measured whenever the sample heater current was changed. Heat pulses were typically 2-8 seconds. The temperature response (conductance) of the thermometer was monitored using a chart recorder connected to the analog output of an S.H.E. conductance bridge. The excitation voltage used for the thermometer was  $100\mu\text{V}$  above 1 K and  $10\mu\text{V}$  below 1 K. The temperature drifts before and after the heat pulse were extrapolated to time  $t=0$  to determine the change in temperature. The duration of the heat pulse was measured with a digital timer. The heat capacity was calculated using the equation

$$C = \frac{\Delta Q}{\Delta T} = \frac{t V_H i}{(T_f - T_i)} = \frac{t V_H V_S}{R_S (T_f - T_i)}$$

where

- $\Delta Q$  = amount of heat applied
- $\Delta T$  = change in temperature
- $t$  = duration of heat pulse
- $V_H$  = voltage drop across the heater
- $V_S$  = voltage drop across the standard resistor
- $i$  = current through the heater
- $T_f$  = final temperature
- $T_i$  = initial temperature
- $R_S$  = resistance of standard resistor

The thermal shield temperature was adjusted in order maintain a temperature equal to that of the sample in order to minimize

the drift of the sample temperature. The analysis of the data was accomplished with the use of existing heat capacity analysis programs on a VAX computer. These programs use subroutines taken from Bevington.<sup>23</sup>

## IV. HEAT CAPACITY OF COPPER AND ADDENDA

## A. Introduction

The initial measurement with the calorimeter was the determination of the addenda heat capacity. Heat capacity of the addenda must be accurately known so that it may be subtracted from the total heat capacity when measuring a sample. The data obtained were fit to an equation of the form

$$C(T) = \sum_{i=1}^N A_i (T/T_{\max})^i$$

with the coefficients being determined from the fit (Table 1 provides the coefficients for addenda 1 and addenda 2). These coefficients were then used in the heat capacity analysis program to subtract the addenda heat capacity from the total heat capacity. The addenda measurements will be discussed in the next section.

Once the addenda heat capacity was characterized, the next measurement consisted of measuring a standard reference material.<sup>24</sup> The 1965 Calorimetry Conference copper standard (sample No. T3-6) was chosen as the standard reference material since it is well established for testing calorimeters between 0.3 K and 25 K. Details of the preparation of the copper standard are described elsewhere.<sup>25</sup> Measurements by many groups have produced the polynomial reference equation for copper (valid for  $0.3 < T < 25$  K) of the form

$$C(T) = \sum_{i=1}^6 A_i T^{2i-1} \text{ mJ/mol K}$$

where 1 mol = 63.54g. The lower limit for using this equation is 0.3 K since there is evidence of a heat capacity anomaly at lower temperatures.<sup>26</sup>

The fit obtained for the standard copper sample had a large percent deviation due to scatter in the data. It was decided that the measurement of another copper sample might clarify the origin of the scatter. A sample of about twice the mass of the calorimetry standard was obtained from Dr. C. A. Swenson. The high purity copper sample was prepared by the Ames Laboratory Materials Preparation Center by electron beam melting 99.999% copper.

After the second measurement of copper, the original addenda was rebuilt. The bellows had not been sufficiently pumped out prior to warming the calorimeter to room temperature resulting in a sudden expansion of the bellows and damaging the addenda. Some additional silver epoxy and varnish were required to repair the addenda. Also the polyimide encapsulation of the strain gauge was removed to ensure better thermal contact between the heater and the sapphire substrate.

The heat capacity of the 1965 Calorimetry Conference copper standard was remeasured as well as the addenda. The results of the copper and addenda measurements are discussed in the next section.

## B. Results and Discussion

Before discussing the copper data, a brief discussion about the addenda measurement is in order. The addenda data have a large amount of scatter. Deviations from the fit in the temperature range from 0.15 K to 1.5 K are on the order of 34%. Some of the scatter is due to experimental technique since the method used to obtain data had not been yet refined. However, the remaining scatter is probably due to other small effects such as external heat leaks. Since the magnitude of the addenda heat capacity is so small at these temperatures, other effects may have been more easily observed. The addenda heat capacity is on the order of  $0.35 \mu\text{J}/\text{K}$  at 0.15 K and approximately  $4 \mu\text{J}/\text{K}$  at 1 K.

The addenda heat capacity was remeasured after it was rebuilt. It is essentially identical to the original addenda heat capacity with the only noticeable difference being an additional contribution above 1 K due to the increased mass of the rebuilt addenda. The addenda heat capacity was subtracted from the measured copper samples and the  $\text{CeSi}_x$  samples in order to determine the sample heat capacity.

The copper data were fit to a polynomial of the form described in the previous section. Table 2 provides the coefficients for the copper reference equation and the measured copper samples. Figure 5 shows a plot of  $C$  versus  $T$  for the copper data and the solid line represents the fit for the



standard reference equation. Some of the scatter observed in the data is probably due to experimental technique rather than lack of precision in the calorimeter electronics. The largest error introduced in this measurement is the determination of the heat pulse height. Also, drifts in the shield temperature could cause drifts in the sample introducing additional error in the measured heat capacity. Figure 6 shows a plot of percent difference versus temperatures of the copper data with respect to the copper reference equation.

The data indicate that the values for the specific heat of the copper sample begin to deviate from the copper reference equation fit at about 0.5 K. This deviation becomes greater as temperature decreases. Possible explanations for this behavior are: (1) the thermometer calibration has changed, (2) the thermometer is becoming thermally decoupled from the substrate (and the sample), (3) self heating or heat leaks through the electrical leads. The first explanation seems unlikely since the "4 K" value has not changed with respect to the other calibrated germanium thermometer. Both thermometers are compared to one another before a measurement run with exchange gas in the vacuum can and liquid  $^4\text{He}$  in the dewar. Both thermometers indicate the same temperature. The second and third explanations are related and are probably the cause of the observed deviation from the fit. The varnish-sapphire-grease-sample boundaries may not be sufficiently thermally conducting at the lowest temperatures. The thermometer may not

Table 1. Addenda Coefficients

	Addenda 1	Addenda 2
A <sub>1</sub>	5.27986788E-05	5.24719756E-04
A <sub>2</sub>	-2.22584578E-03	-1.50630611E-03
A <sub>3</sub>	1.97980452E-02	-1.47946767E-02
A <sub>4</sub>	6.47463630E-02	8.13692147E-02
A <sub>5</sub>	-1.39625857E-01	-9.35226738E-02
A <sub>6</sub>	6.99987479E-02	3.61105260E-02

Table 2. Copper Coefficients

	Copper Equation	Ames Lab Copper	1965 Copper
A <sub>1</sub>	6.9434E-01	1.7684E-01	1.3060E-01
A <sub>2</sub>	4.7548E-02	2.3053E+00	1.7442E+00
A <sub>3</sub>	1.6314E-06	-3.2650E+00	-1.7504E+00
A <sub>4</sub>	9.4786E-08	1.9705E+00	8.2205E-01
A <sub>5</sub>	-1.3639E-08	-5.1644E-01	-1.7375E-01
A <sub>6</sub>	5.3898E-14	4.8792E-02	1.3437E-02

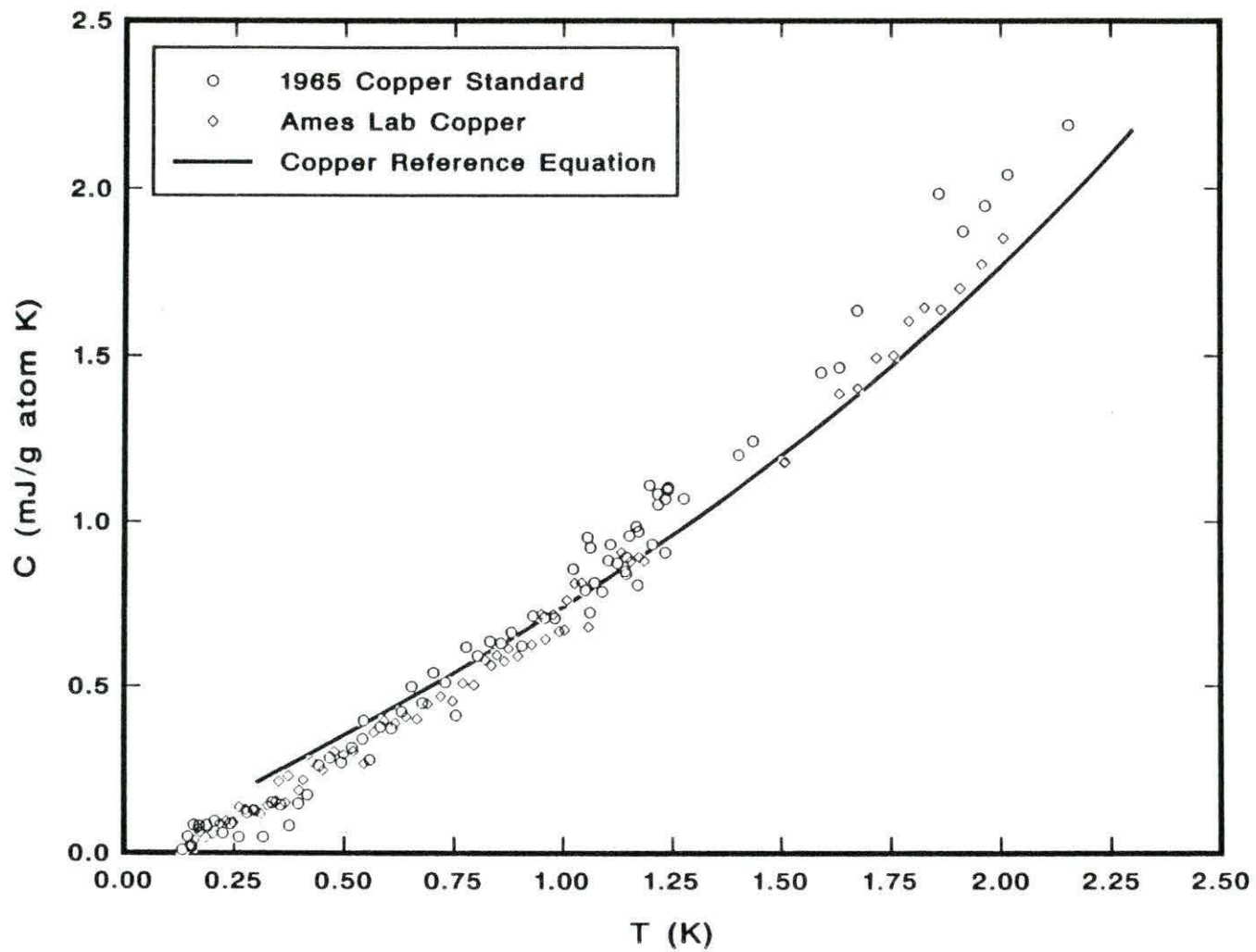


Figure 5.  $C$  versus  $T$  for the 1965 copper standard and the Ames Lab copper sample. The solid line indicates the copper reference equation fit

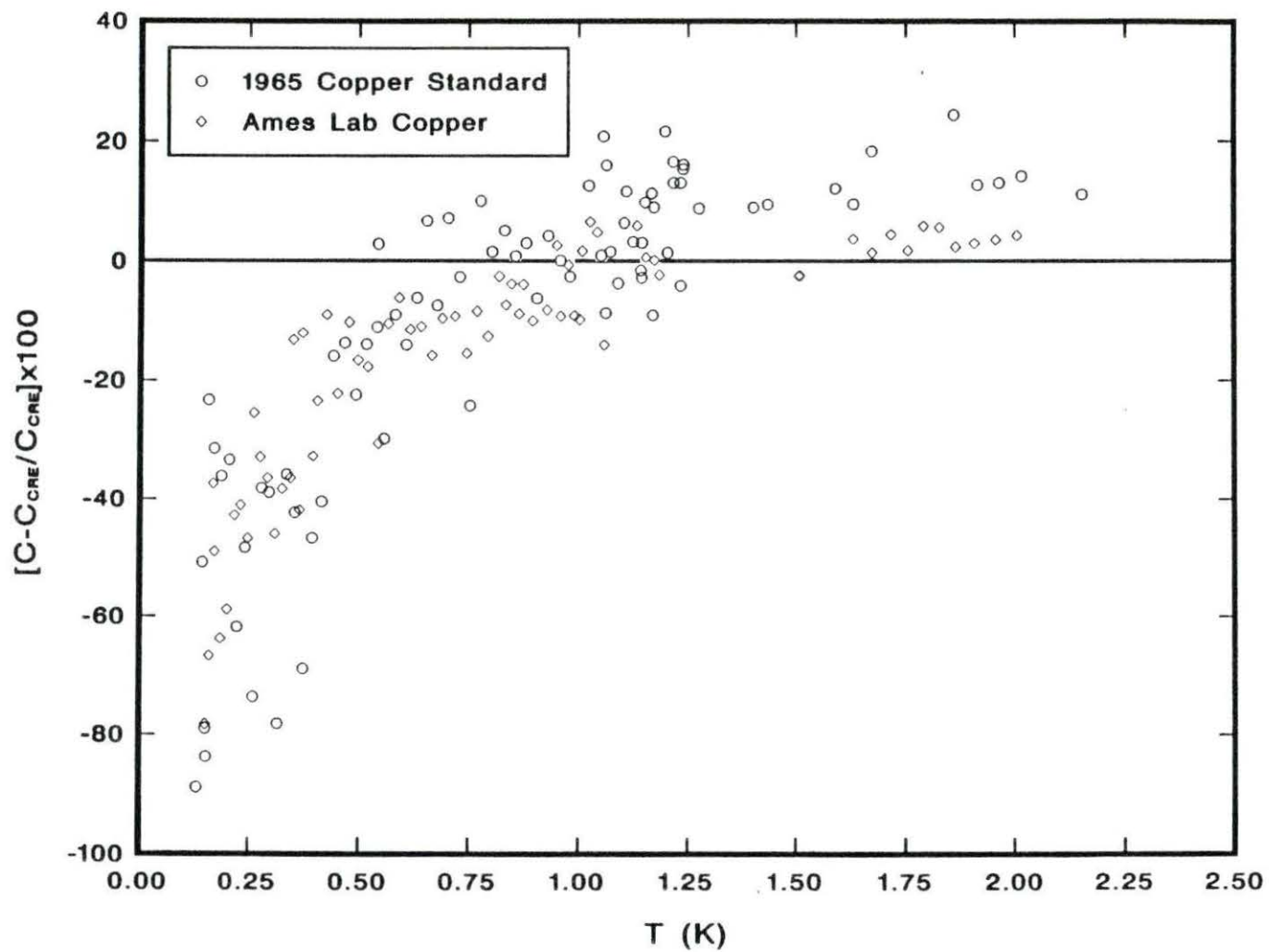


Figure 6.  $[C-C_{CRE}/C_{CRE}] \times 100$  versus  $T$  for both copper samples. The plot indicates the percent difference between the data and the copper reference equation

be in good thermal equilibrium with the sample. If the thermometer is decoupled from the substrate, it may be more susceptible to self heating. At the lowest temperatures, even the smallest excitation voltages may cause self heating in the thermometer if the thermometer or thermometer leads are not properly grounded (thermally). Probably the best solution would be to calibrate the thermometer in situ so that any discrepancies due to thermal contact are accounted for in the calibration. This would only work if the time constants involved are not exceedingly long. These explanations do not take into account any problems associated with vibrational heating. Although there is some vibrational heating, it is believed to be negligible since the data seem to indicate that the thermometer and not the sample are at a higher temperature.

V. HEAT CAPACITY OF  $\text{CeSi}_{1.850}$  AND  $\text{CeSi}_{1.855}$ 

## A. Introduction

In order to understand the nature of the nonmagnetic to magnetic transition in the  $\text{CeSi}_x$  ( $1.60 \leq x \leq 2.00$ ) system, heat capacity was measured on samples with compositions near the critical region ( $x \sim 1.85$ ). The alloys  $\text{CeSi}_{1.850}$  and  $\text{CeSi}_{1.855}$  were chosen.

The  $\text{CeSi}_{1.850}$  sample was chosen since previous data (ac susceptibility) indicated that there may be some kind of magnetic ordering at 1 K. Heat capacity measurements would indicate whether or not this observed ordering at 1 K is a bulk effect. The  $\text{CeSi}_{1.855}$  was chosen since its composition coincides with an observed anomaly in the room temperature resistivity. It has been suggested that this anomaly is due to the onset of magnetic ordering.<sup>27</sup> The heat capacity of  $\text{CeSi}_{1.855}$  to low temperatures would determine if there is a correlation between the peak in room temperature resistivity and the onset of magnetic ordering.

## B. Experimental Details

The metallic alloys used for heat capacity measurements had the composition  $\text{CeSi}_{1.850}$  and  $\text{CeSi}_{1.855}$ . The alloys were prepared by arc melting stoichiometric amounts of Ce and Si in

a gettered atmosphere of argon. Mass losses were  $<0.3\%$  and the typical mass of the samples was approximately 15 grams. The purity of the starting materials is listed in Appendix B. The arc melted ingots were drop cast into right circular cylinders. The samples were then sealed in Ta crucibles and vacuum annealed for 14-18 days at  $1100^{\circ}\text{C}$ . After the annealing time, the furnaces were turned off and the samples were allowed to cool to room temperature ( $\sim 1$  hour). Metallographic examination revealed the alloys to be homogeneous and single phase.

Powder x-ray diffraction patterns of the samples indicated that they had the tetragonal  $\alpha\text{-ThSi}_2$  type structure. No impurity reflections were observed in the x-ray pattern.

The heat capacity of both the  $\text{CeSi}_{1.850}$  and  $\text{CeSi}_{1.855}$  were measured in the temperature range 150 mK to 1.5 K using the calorimeter described in Section II. For the temperature range 1.5 K to 20 K, the heat capacity was measured by a semi-adiabatic, heat pulse technique using a calibrated germanium thermometer to monitor the temperature.<sup>28</sup>

### C. Results and Discussion

The data for  $\text{CeSi}_{1.850}$  are presented in Figures 7-10. Figures 7 and 8 are plots of  $C$  versus  $T$  while Figures 9 and 10 are plots of  $C/T$  versus  $T^2$ . The data for  $\text{CeSi}_{1.855}$  are presented in Figures 11-14 and include the forementioned plots. The plots show two sets of data taken with two different

calorimeters. The open circle data points are data obtained in this study. The solid circle data points represent data obtained with a semi-adiabatic calorimeter in the temperature range 1.5 K to 20 K (see reference 28).

The data indicate that both  $\text{CeSi}_{1.850}$  and  $\text{CeSi}_{1.855}$  do not order magnetically. The plots of  $C$  versus  $T$  show a linear decrease in the heat capacity as the temperature approaches zero. At the lowest temperatures, some deviation from the linear fit is observed. This deviation is probably due to the inaccurate thermometer reading (as discussed in Section IV).

The two sets of data for  $\text{CeSi}_{1.850}$  show good agreement. Fitting the data between 1.5 K and 0.6 K to a linear term yields a value of  $89.17 \text{ mJ/g atom K}^2$  for the electronic specific heat coefficient.

The two data sets for  $\text{CeSi}_{1.855}$  do not have good agreement but do exhibit approximately the same temperature dependence. The data for the larger sample may be in error due to problems with the calorimeter. The sample will be remeasured. The electronic specific heat coefficient for  $\text{CeSi}_{1.855}$  is  $86.55 \text{ mJ/g atom K}^2$ .



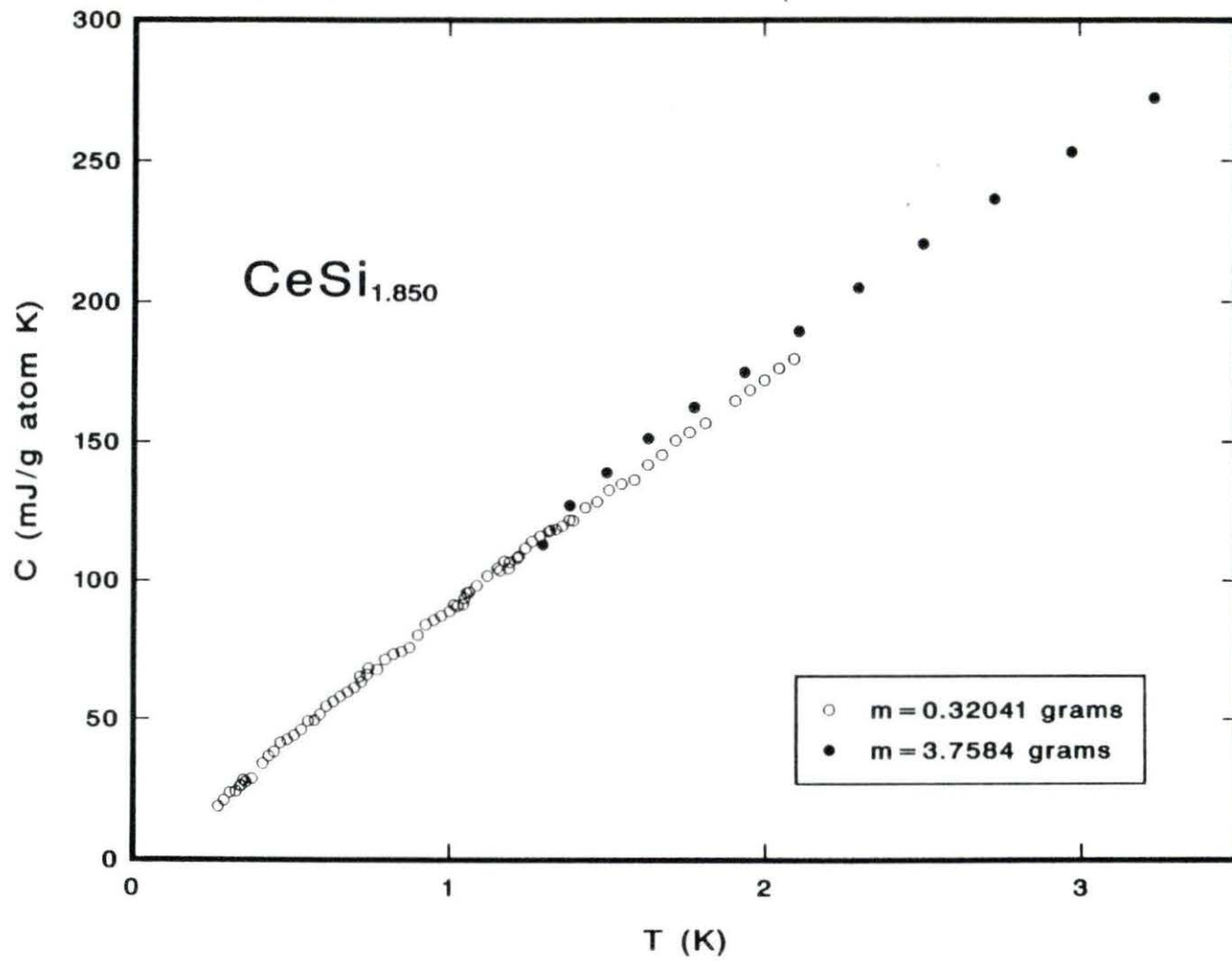


Figure 7. C versus T for CeSi<sub>1.850</sub> for the temperature range 0 < T < 3.5 K

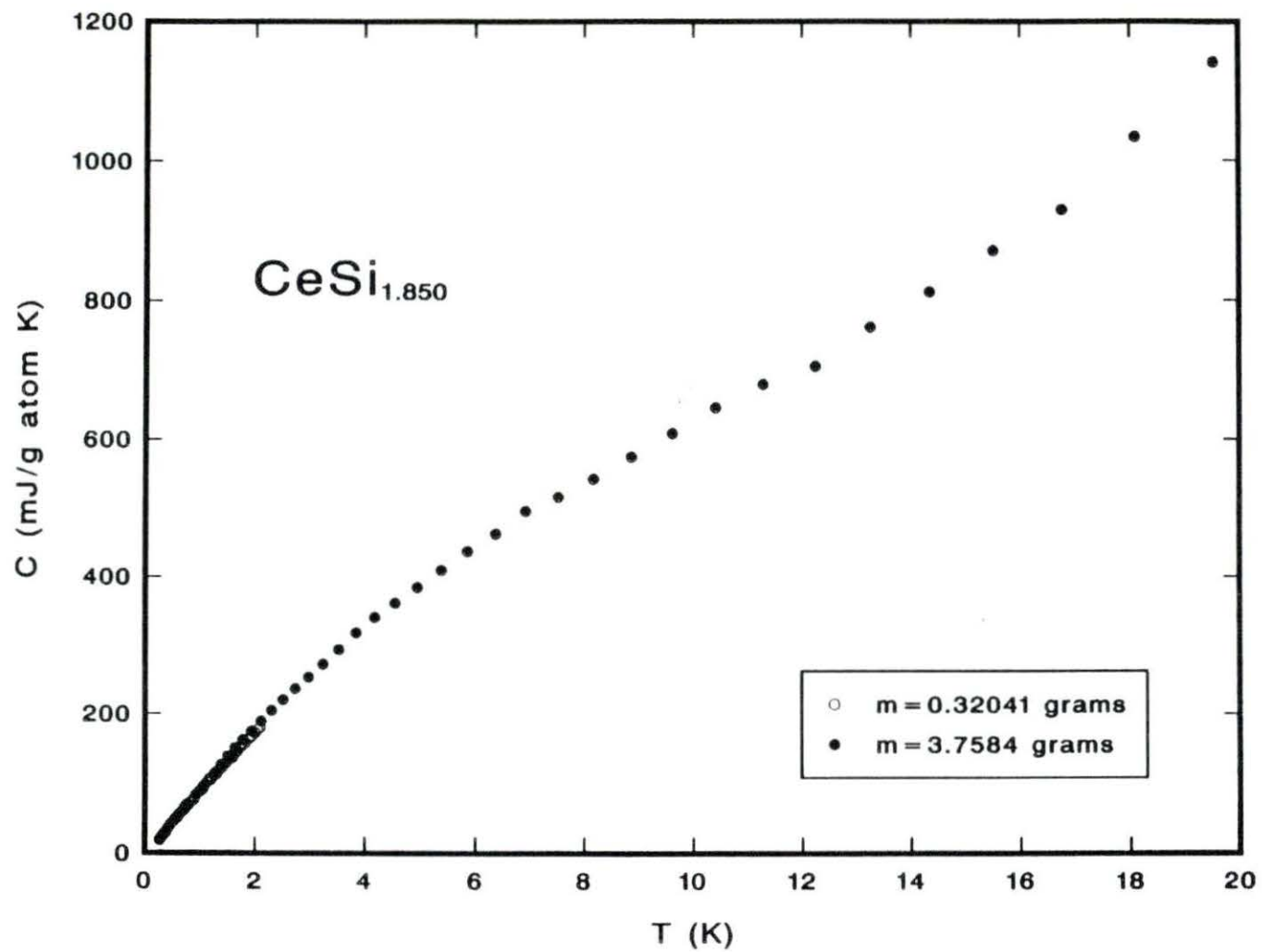


Figure 8. C versus T for CeSi<sub>1.850</sub> for the temperature range 0 < T < 20 K

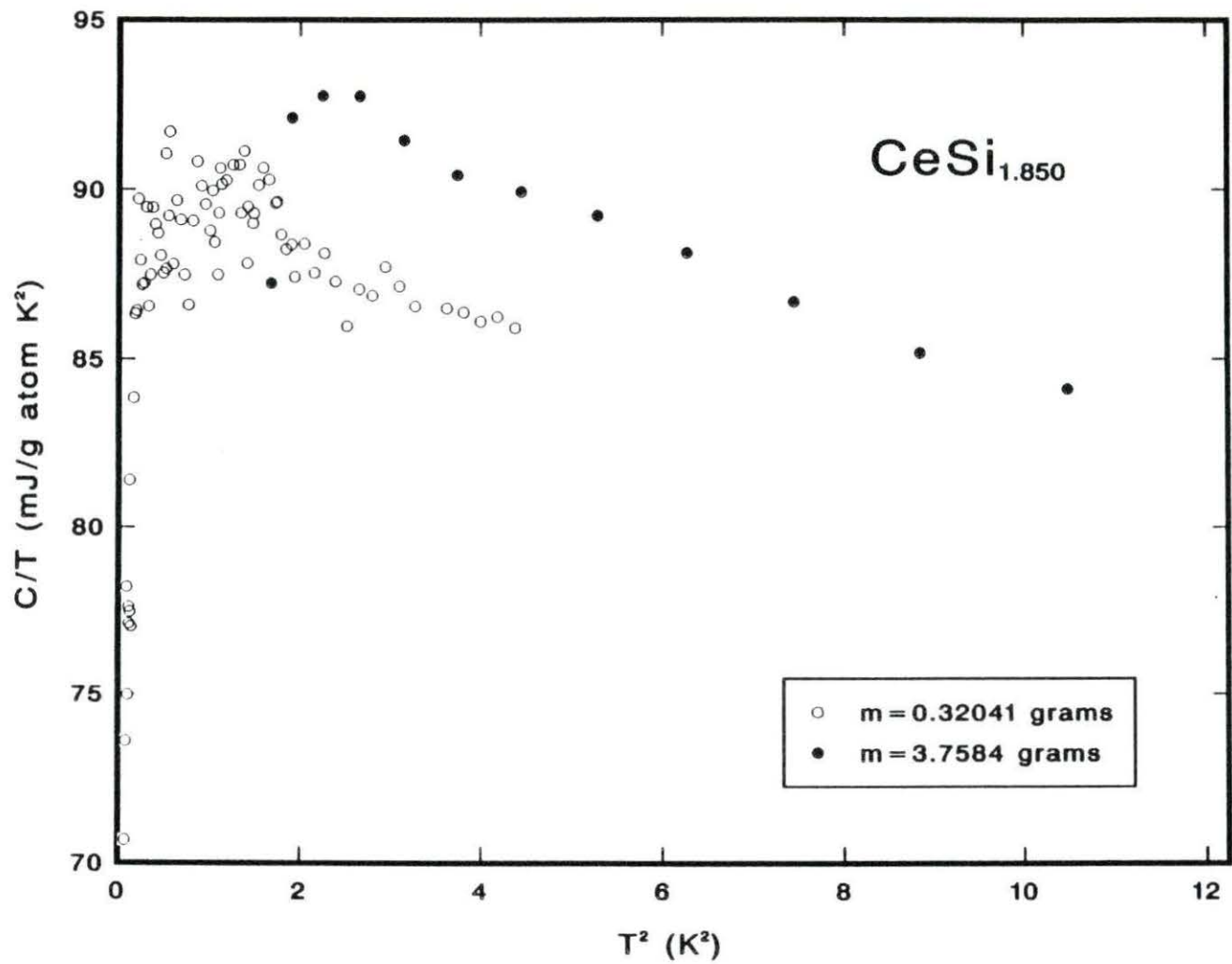


Figure 9. C/T versus  $T^2$  for CeSi<sub>1.850</sub> for the temperature range  $0 < T < 3.5$  K

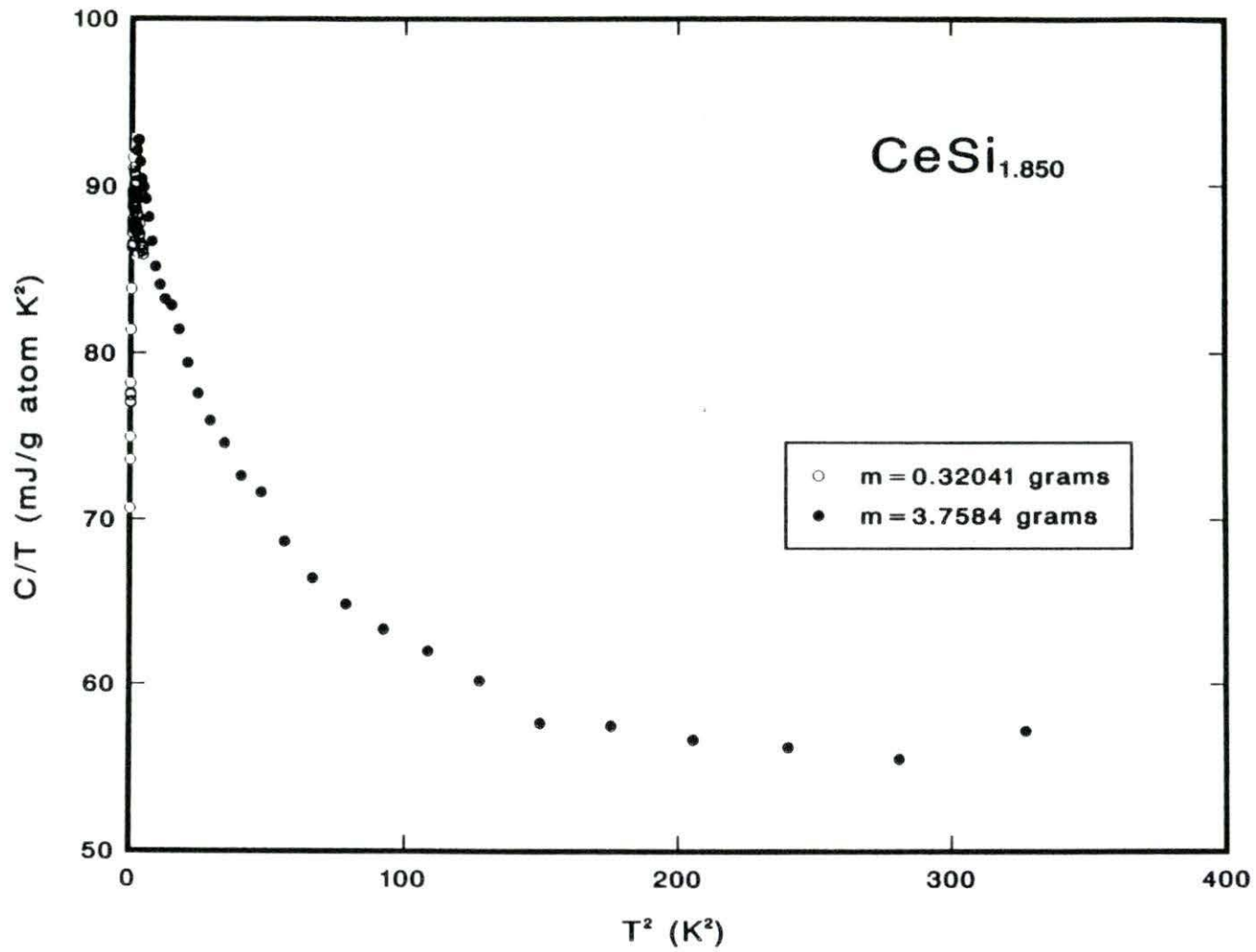


Figure 10. C/T versus T<sup>2</sup> for CeSi<sub>1.850</sub> for the temperature range 0 < T < 20 K

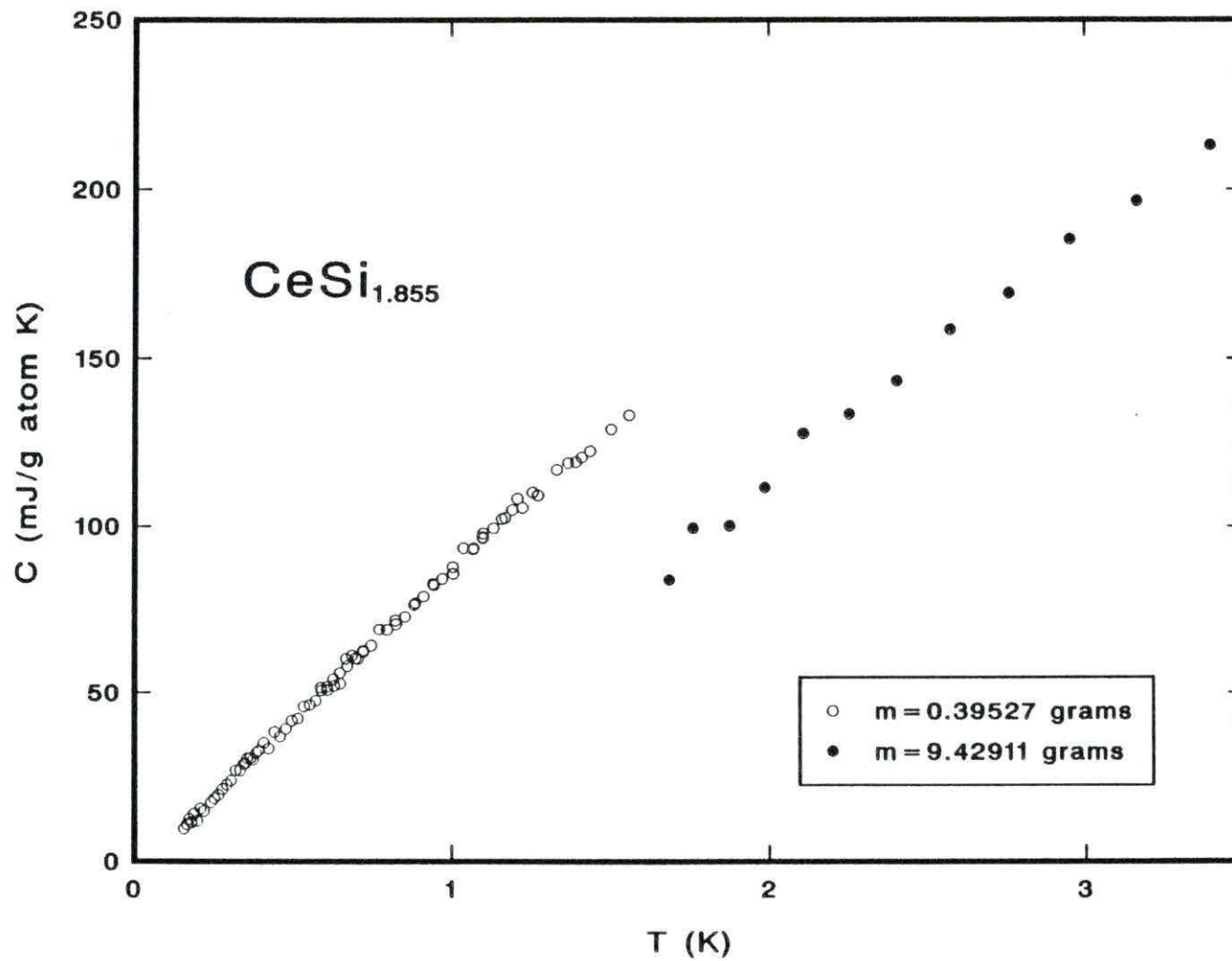


Figure 11. C versus T for CeSi<sub>1.855</sub> for the temperature range 0 < T < 3.5 K

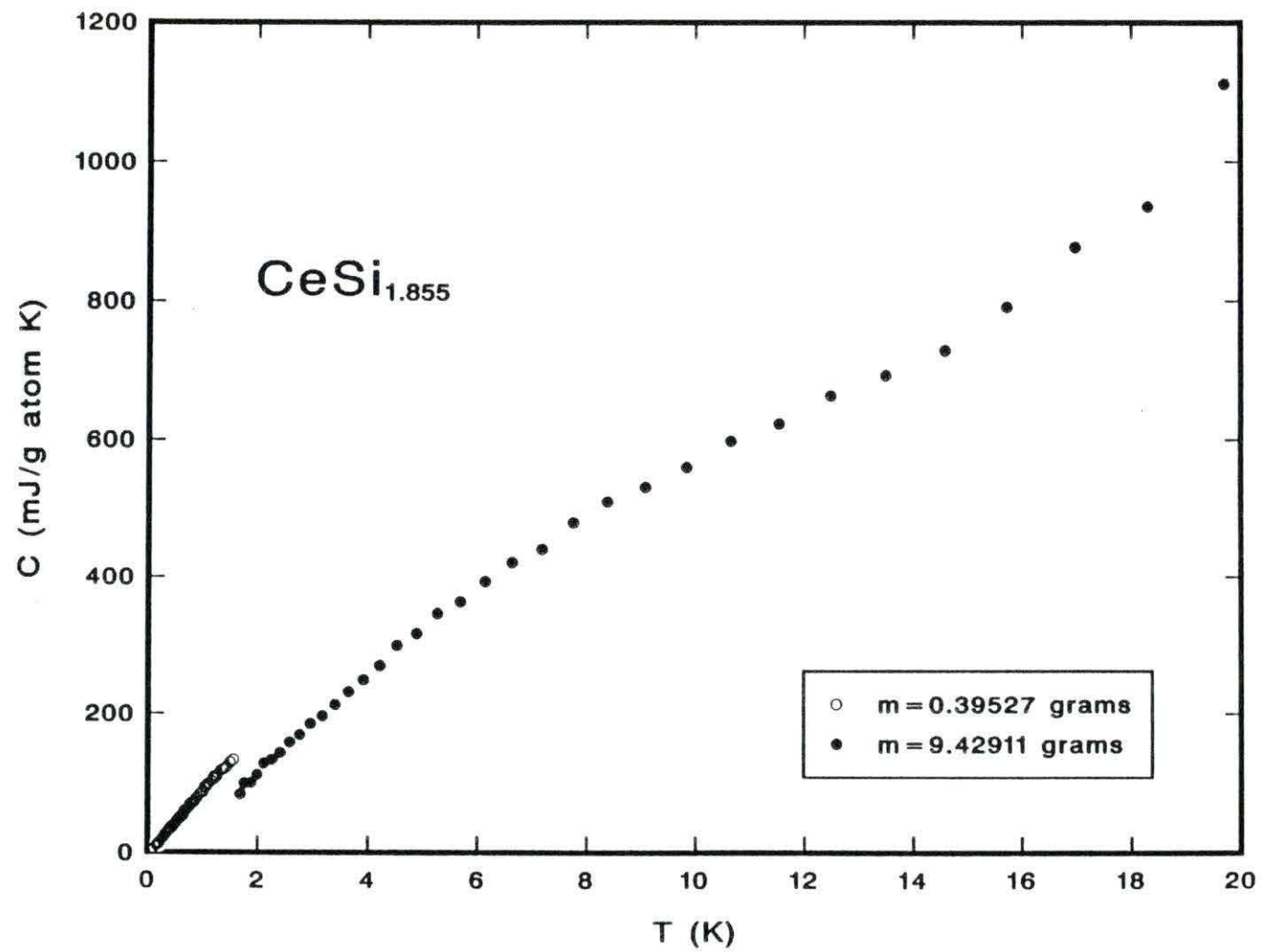


Figure 12.  $C$  versus  $T$  for  $\text{CeSi}_{1.855}$  for the temperature range  $0 < T < 20$  K

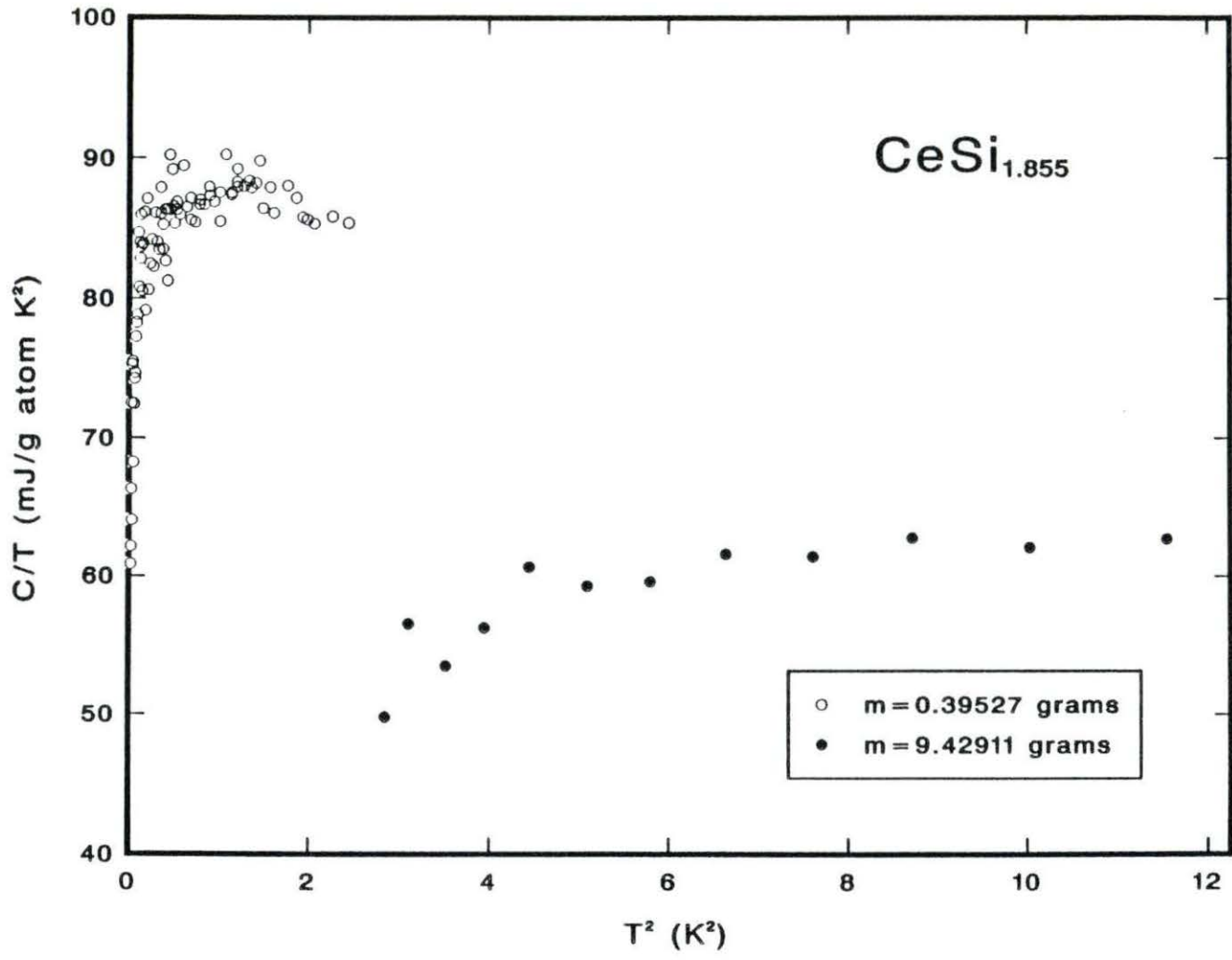


Figure 13. C/T versus T<sup>2</sup> for CeSi<sub>1.855</sub> for the temperature range 0 < T < 3.5 K

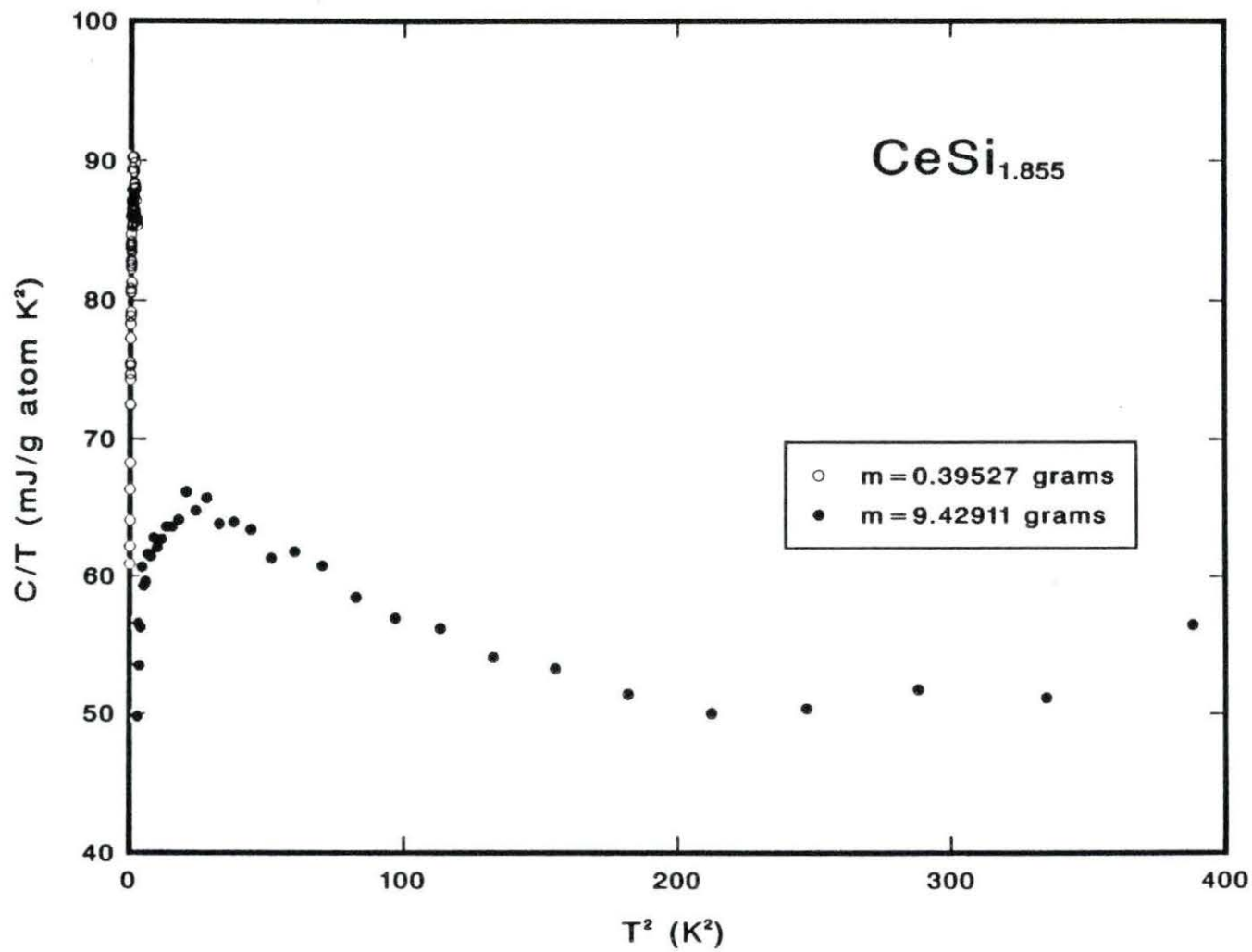


Figure 14. C/T versus  $T^2$  for CeSi<sub>1.855</sub> for the temperature range  $0 < T < 20$  K



## VI. SUMMARY AND CONCLUSIONS

## A. Calorimeter Design

The calorimeter proved to operate as anticipated with only some minor difficulties. Some problems were encountered with the heat switch and the addenda.

The bellows heat switch operated in the manner described previously. However, the problems associated with vibrational heating made its use below 0.5 K very difficult. When it was used to cool the sample to 180 mK, the vibrational heating upon isolation would warm the sample to 250 mK. Also, overpressurizing the bellows could result in breaking the nylon support threads. Insufficient pumping of the bellows prior to warming the calorimeter above 4 K proved to be disastrous. A bellows of similar design could be made practical for calorimeters operating above 0.5 K.

The other problem encountered was with the addenda. Thermal barriers between the thermometer and the sample seemed to decouple one from the other. This resulted in discrepancies in the measured heat capacity. To correct for this problem, the thermometer should probably be calibrated in situ. This may resolve the problem if the time constants involved are not greater than a few seconds.

The mass and size of the calorimeter (mounting flange, addenda holder, and thermal shield) could be reduced. A

smaller mass of copper would be easier to cool to the lowest temperature of the dilution refrigerator. All dimensions of the calorimeter could be reduced.

#### B. $\text{CeSi}_x$ Metallic Alloys

The alloys  $\text{CeSi}_{1.850}$  and  $\text{CeSi}_{1.855}$  were measured and no ferromagnetic ordering was observed down to about 0.150 K. To clarify the nature of the magnetic state in the  $\text{CeSi}_x$  system, more measurements (of the lower silicon concentration alloys) will need to be made. Heat capacity measurements combined with resistivity and ac susceptibility data should give a better understanding of the magnetic states in the  $\text{CeSi}_x$  system.

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## VIII. ACKNOWLEDGEMENTS

I would like to thank my major professor Dr. Karl A. Gschneidner, Jr. for his advice and guidance during my graduate career. His insight into metallurgy and solid state physics has been most helpful in my research as well as in the classroom. I also thank Professor Gschneidner for providing the samples for this work.

A sincere thank you to Dr. John D. Verhoeven for serving on my graduate committee. His excellent teaching first captured my interest in metallurgy. I shall always remember his comparison of heterogeneous nucleation in metals to that of CO<sub>2</sub> bubbles nucleating in a glass of beer.

Dr. Robert N. Shelton deserves special thanks. He has been the key person in the development of my scientific and technical abilities. I can never thank him enough.

I would also like to thank Dr. Bill McCallum and Dr. Clayton Swenson for useful discussions concerning calorimeter design.

Former graduate students Dr. W. H. Lee, Dr. H. D. Yang, Dr. Y. Xu, Dr. K. S. Athreya, and Dr. L. S. Hausermann-Berg deserve thanks for their helpful discussions, encouragement, and friendship during my graduate career.

I am grateful for the friendship and humor of Charles Hewitt, Karl Lichtenberger, and Steve Sanders. I especially thank Charles for his help with my computer related questions.

Postdoctoral Associate Dr. Susan Kauzlarich is responsible for the quality of the graphics in this thesis. Her endless patience and encouragement during the final months of this work have been greatly appreciated.

So many more people deserve acknowledgement. However, to keep this section shorter than the introduction, I will simply say thank you to the faculty, staff, technicians, and graduate students of Ames Laboratory/Iowa State University with whom I have had the opportunity to work with. The last five years have been rewarding.

Finally I wish to thank my parents, Janis and Alma. They have been a source of encouragement during my undergraduate and graduate career. I could not have accomplished so much without their love and support.

## IX. APPENDIX A: GOLD PLATING

In the temperature range below 1 K, oxide layers act as thermally insulating barriers. It is therefore desirable to prevent oxide formation on contact surfaces. For copper metal, a relatively easy method to prevent oxide formation is to gold plate the surfaces. A procedure and chemical plating solution are described below. Also some safety precautions relating to the use of cyanide solutions are mentioned.

## A. Cyanide Gold Plating Bath

Potassium Gold Cyanide[KAu(CN) <sub>2</sub> ]	12.3 grams
Potassium Cyanide[KCN]	14.3 grams
Potassium Hydroxide[KOH]	19.4 grams
Potassium Sulfite[K <sub>2</sub> SO <sub>3</sub> ]	9.7 grams
Distilled or deionized water	1.0 liter

Anode: 24 K gold sheet or wire

Cathode: Object to be gold plated

Temperature: Bath temperature 25-70 °C

Current density: 0.01-100 mA/cm<sup>2</sup>

Time: Several minutes-dependant on current density

Storage: Clean, nonmetallic container



## B. Procedure For Gold Plating Copper

1. Be familiar with the hazards of working with cyanide solutions. Cyanide is potentially lethal. All work should be done in a vented hood.
2. Clean surfaces to be plated thoroughly. If surface oxides and fingerprints are not removed, these areas will not plate. Surfaces can be cleaned with acetone or methanol to remove grease and can be etched with dilute nitric acid to remove oxide layer.
3. The object to be plated is the cathode. The gold anode and object are suspended in the bath before the current is applied.
4. The current is slowly increased. The current will depend upon the size of the object being plated. Maintain current densities between  $0.01\text{--}100\text{ mA/cm}^2$ . Lower currents will produce thinner plates.
5. When the object is plated, turn off the current, remove the object from the plating solution, and immerse in water. Thoroughly rinse the gold plated object. After drying, the object can be lightly buffed and replated if a thicker plating is desired.

### C. Safety Precautions For Using Cyanide Solutions

1. Never allow cyanide or cyanide solutions to come into contact with acidic liquids. The combination of the two may produce highly poisonous prussic acid gas.
2. Cyanide baths emit hydrocyanic acid gas which is potentially lethal. Adequate ventilation is required. All work should be done in a vented hood.
3. It is best to use cyanide baths at lower temperatures since less gas is evolved.
4. Avoid skin contact, inhalation of cyanide dust, or ingestion of cyanide. Wear protective gloves, clothing, and eye protection when working with cyanide baths. Cyanide solutions can penetrate the skin and exposure can be potentially lethal.

X. APPENDIX B: SOURCES AND PURITIES OF  
STARTING MATERIALS

Cerium was prepared at the Materials Preparation Center of the Ames Laboratory. The major impurities (atomic ppm) greater than 1 ppm are listed below.

<u>Impurity</u>	<u>Ames Lab Ce-11480</u>	<u>Ames Lab Ce-42683</u>
H	not detectable	693
C	105	70
N	80	200
O	648	228
F	125	88
Na	< 2	9
Al	4	< 0.5
Si	30	< 9
Cl	20	20
Ca	< 2	2.9
Fe	< 7.5	3
Ni	10	6.6
Cu	5.1	2.6
Y	0.6	1.3
La	< 1	2.9
Tb	< 1	4
Ta	45	7.6
Pt	14	16

Silicon was purchased from Dow Corning Corporation. The silicon was semiconductor grade with room temperature resistivity greater than 1000 ohm-cm.

## XI. HEAT CAPACITY DATA

## A. Ames Lab Copper Data

T (K)	C (mJ/g atom K)
0.15078	2.278225E-02
0.15868	3.676232E-02
0.16753	7.293118E-02
0.17087	6.072209E-02
0.18504	4.666542E-02
0.20083	5.760079E-02
0.21718	8.653146E-02
0.23062	9.476000E-02
0.24821	9.225803E-02
0.26148	1.359200E-01
0.27646	1.294599E-01
0.29286	1.299054E-01
0.30983	1.171186E-01
0.32623	1.409051E-01
0.34555	1.537941E-01
0.35159	2.137798E-01
0.36604	1.490232E-01
0.37276	2.298591E-01
0.39631	1.869760E-01
0.40616	2.183323E-01
0.42696	2.731472E-01
0.45154	2.473363E-01
0.47757	3.023302E-01
0.49798	2.933350E-01
0.52061	3.031060E-01
0.54428	2.675784E-01
0.56737	3.603885E-01
0.59166	3.947363E-01
0.61649	3.887201E-01
0.64105	4.073138E-01
0.66601	4.012358E-01
0.69021	4.472052E-01
0.71918	4.693577E-01
0.74681	4.551384E-01
0.76997	5.097518E-01
0.79512	5.034505E-01
0.82059	5.810275E-01
0.83564	5.634530E-01
0.84792	5.942205E-01
0.86601	5.765556E-01
0.87541	6.149719E-01

0.89711	5.916803E-01
0.92873	6.271242E-01
0.95120	7.198595E-01
0.96016	6.435819E-01
0.97795	7.187091E-01
0.99139	6.674928E-01
1.00350	6.718740E-01
1.00900	7.618717E-01
1.02620	8.139892E-01
1.04270	8.154390E-01
1.05920	6.807734E-01
1.13400	9.075725E-01
1.15460	8.801374E-01
1.17450	8.940039E-01
1.18600	8.821283E-01
1.50700	1.179576E+00
1.50880	1.181753E+00
1.63050	1.387279E+00
1.67320	1.403985E+00
1.71600	1.495197E+00
1.75530	1.502090E+00
1.79060	1.604894E+00
1.82660	1.645640E+00
1.86350	1.639370E+00
1.90690	1.703008E+00
1.95600	1.775182E+00
2.00530	1.852120E+00

## B. 1965 Calorimetry Conference Copper Data

T (K)	C (mJ/g atom K)
0.13094	1.015935E-02
0.14311	4.901393E-02
0.15046	2.198990E-02
0.15225	1.720435E-02
0.15643	8.347040E-02
0.16983	8.096904E-02
0.18667	8.299317E-02
0.20492	9.506491E-02
0.22351	5.951712E-02
0.24159	8.710099E-02
0.26069	4.792992E-02
0.27915	1.204835E-01
0.29646	1.265711E-01
0.31620	4.823413E-02
0.33627	1.509164E-01
0.35523	1.435162E-01
0.37485	8.175377E-02
0.39519	1.479827E-01
0.41598	1.739650E-01
0.44194	2.615549E-01
0.46734	2.842551E-01
0.49327	2.701775E-01
0.51691	3.145530E-01
0.54159	3.411422E-01
0.54385	3.961936E-01
0.55798	2.776742E-01
0.58287	3.768938E-01
0.60778	3.720563E-01
0.63141	4.225905E-01
0.65408	4.988635E-01
0.67830	4.497624E-01
0.70291	5.408092E-01
0.72999	5.113733E-01
0.75415	4.123041E-01
0.77789	6.190720E-01
0.80421	5.922681E-01
0.83227	6.361058E-01
0.85739	6.306631E-01
0.88184	6.643463E-01
0.90596	6.232210E-01
0.93140	7.140927E-01
0.95925	7.088344E-01
0.98124	7.072434E-01
1.02310	8.573306E-01
1.05130	7.928244E-01

1.05610	9.536295E-01
1.06210	7.253258E-01
1.06300	9.225395E-01
1.07230	8.157475E-01
1.09020	7.883065E-01
1.10420	8.837271E-01
1.10890	9.319812E-01
1.12440	8.755900E-01
1.14270	8.507746E-01
1.14460	8.421858E-01
1.14530	8.934490E-01
1.15220	9.584504E-01
1.16760	9.866631E-01
1.17100	8.090158E-01
1.17330	9.714970E-01
1.19850	1.111805E+00
1.20470	9.325904E-01
1.21690	1.085103E+00
1.21780	1.053145E+00
1.23380	1.069722E+00
1.23420	9.076872E-01
1.23960	1.097469E+00
1.24030	1.105292E+00
1.27600	1.071515E+00
1.40150	1.202944E+00
1.43520	1.244865E+00
1.58930	1.451162E+00
1.63100	1.466316E+00
1.67170	1.636551E+00
1.85900	1.985572E+00
1.91390	1.873569E+00
1.96400	1.949354E+00
2.01560	2.042730E+00
2.15330	2.189744E+00

## C. CeSi 1.850 Data

T (K)	C (mJ/g atom K)
0.26748	18.90395
0.28539	21.00422
0.30413	23.78474
0.32329	24.23736
0.33663	26.12556
0.33988	26.20739
0.34679	28.22983
0.35450	27.46082
0.37311	28.73541
0.40718	34.14397
0.42558	36.74372
0.44270	38.26393
0.46345	41.58246
0.48519	42.65797
0.50662	44.17586
0.52951	46.20116
0.55154	49.34937
0.57279	49.58225
0.58995	51.61214
0.61053	54.62534
0.63293	56.31544
0.65551	58.15288
0.67862	59.75779
0.70046	61.31702
0.71776	65.35761
0.72234	63.32740
0.73999	66.02600
0.74509	68.32719
0.77286	67.86197
0.79723	71.49537
0.82427	73.45274
0.84927	74.30109
0.87506	75.78098
0.90138	80.29516
0.92603	84.11095
0.95149	85.74088
0.97427	87.26383
1.00080	88.85814
1.01440	91.26432
1.02590	90.74120
1.04390	91.33193
1.04870	93.66200
1.05450	95.57243
1.06380	95.91603
1.08760	98.18733



1.12090	101.69997
1.15250	104.56691
1.16040	103.63766
1.17460	107.04920
1.18880	104.41004
1.19200	106.67604
1.21520	108.16446
1.21960	108.91165
1.23990	111.75189
1.26010	114.21386
1.28600	116.11584
1.31410	117.74870
1.31930	118.26137
1.33730	118.57927
1.35760	119.79456
1.38020	121.97169
1.39270	121.75719
1.43080	126.48404
1.46920	128.61632
1.50690	132.78477
1.54700	135.03131
1.58780	136.50272
1.63030	141.93607
1.67470	145.48007
1.71790	150.68738
1.76240	153.58226
1.81190	156.82860
1.90590	164.85011
1.95320	168.71870
2.00010	172.22723
2.04610	176.46565
2.09260	179.79298

D. CeSi<sub>1.855</sub> Data

T (K)	C (mJ/g atom K)
0.15540	9.66004
0.16470	10.92350
0.17185	12.46229
0.17870	11.44715
0.18657	14.04424
0.19661	11.96742
0.20702	15.62928
0.21827	14.89712
0.24104	17.46586
0.25074	18.62141
0.26330	19.66202
0.27629	21.34463
0.28996	22.69716
0.30306	23.88840
0.31785	26.92349
0.33272	26.88868
0.34299	28.80735
0.34886	28.89833
0.35485	30.50475
0.36498	30.54888
0.37348	30.07875
0.38347	32.16016
0.39120	32.82457
0.40732	35.09082
0.42254	33.44375
0.44066	38.38830
0.45843	36.95699
0.47700	39.33828
0.49579	41.73832
0.51494	42.36865
0.53421	46.00203
0.55314	46.47881
0.57141	47.69939
0.58774	51.66185
0.58963	50.73321
0.60794	51.83356
0.60929	50.88249
0.62771	54.19916
0.63042	52.11755
0.64797	55.95237
0.64960	52.78357
0.66772	60.23993
0.67245	58.03303
0.68715	61.28469
0.69822	60.43296

0.70581	60.23565
0.72200	62.72634
0.72225	62.35048
0.74730	64.26270
0.77218	69.08315
0.79730	68.98045
0.82327	71.76399
0.82469	70.58529
0.85302	72.87965
0.88190	76.45212
0.88507	77.03177
0.91141	79.02529
0.94105	82.78084
0.94390	82.43064
0.97048	84.33541
1.00320	87.85432
1.00420	85.86364
1.03610	93.51541
1.06640	93.20417
1.06810	93.54617
1.09630	96.82684
1.09680	96.48056
1.09780	97.96882
1.13090	99.53337
1.15710	102.27758
1.16790	102.66662
1.18990	104.97923
1.20670	108.39446
1.22210	105.63309
1.25360	110.23814
1.27020	109.37331
1.32950	117.05930
1.36550	119.04196
1.39110	119.34943
1.40970	120.72287
1.43690	122.63100
1.50390	129.11159
1.56110	133.30101