

Low-temperature Specific Heat of Platinum using Relaxation Methods

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Abstract

The specific heat of platinum was measured using the non-adiabatic relaxation method at temperatures between 5 K and 16 K. Linear and cubic term results are compared with those of Martin and Gleeson *et al* and are within 10% accuracy.

I. INTRODUCTION

Low temperature specific heat data are integral measurements in physics, chemistry, biology, and medicine. In 1902, Gaede developed the technique of low temperature specific heat measurements. Nernst and Eucken in 1910 furthered this technique with their development of a modern adiabatic low-temperature calorimeter. In 1922, Keesom and Van den Ende developed a very sensitive phosphor-bronze thermometer [1].

In this paper, I describe the experimental procedures used in determining the specific heat of platinum at temperatures between 5 K and 16 K. I determined the specific heat by heating a 145.37 mg sample of platinum through non-adiabatic relaxation methods. The purpose of this experiment at the University of Florida is to provide experience so that I may perform a similar experiment on low-dimensional antiferromagnets with the addition of a high magnetic field at the National High Magnetic Field Lab in Tallahassee, Florida.

In the following sections, I introduce the uses and importance of platinum and specific heat, our experimental methods, data analysis, results, and conclusions.

II. PLATINUM

A. History

Don Antonio Ulloa, officer and scientist, is credited as the first European to mention platinum in his novel published in 1748¹. The Spanish Conquistadors, however, are also credited with finding platinum during the 17th century while searching for gold in the Choco region of Columbia. Julius Caesar Scalinger also found platinum in 1557, but specimens of the metal were not sent to Europe until the mid-18th century [2].

B. Uses of Platinum

Platinum's many applications can be found in jewelry, wire, hard disks, lab vessels, electrical contacts, and coating for missile nose cones and jet engine fuel nozzles. Platinum is considered the most valuable of the precious metals because of its many industrial uses. Platinum is used as a catalyst in the production of petroleum, in fuel cells, and in autocatalysts (a converter that prevents car exhaust from harming the environment) [3]. Many of platinum's uses involve reliability at high temperatures. These uses demand that platinum be extensively studied. Platinum was chosen for the experiment because it does not react with air and its specific heat is accurately known.

¹ D.A. Ulloa, *Relacion historica del viage a la America Meridional hecho de orden de S. Mag*, (Madrid 1748).

III. SPECIFIC HEAT OF METALS

Specific heat is an important physical quantity because of its direct relation to entropy. Entropy is related to the internal energy of a substance. Internal energy in a magnetic field is a function of entropy and magnetization. Because there is no way to measure entropy directly, specific heat is used to determine the entropy. Entropy's application in the real world can be found in engines, refrigerators, air conditioners, and heat pumps [4]. The specific heat (C) is related to entropy (S) via the equation:

$$C = T \left(\frac{\partial S}{\partial T} \right)_H \quad (1)$$

Therefore, S can be obtained by the integration:

$$S = \int_0^T \frac{C(T')}{T'} dT' \quad (2)$$

The overall specific heat equation for metals contains a linear and cubic part:

$$C = \gamma T + \beta T^3 \quad (3)$$

The linear term represents the electron specific heat, characterized by the Fermi temperature, and the cubic term represents the phonon specific heat, characterized by the Debye temperature.

The Fermi energy refers to the highest occupied quantum state in a fermion (a particle that obeys the Fermi-Dirac statistics and has half-integer spin) at absolute zero temperature. The Fermi temperature (T_F) is associated with the Fermi energy (E_F) as shown in Eq. (4) where k is Boltzmann's Constant:

$$E_F = kT_F \quad (4)$$

The Fermi temperature is related to the linear term through Eq. (5):

$$\gamma = \frac{2}{3} \pi^2 k^2 N(E_F) \quad (5)$$

The Debye temperature (θ_D) is a parameter that characterizes the lattice vibrations (phonons) in a solid. It is related to the coefficient of the cubic term through:

$$\beta = \frac{12\pi^4 R}{5\theta_D^3} \quad (6)$$

$N(E_F)$ is the so-called density of states at the Fermi Energy, and R is the ideal gas constant. Some typical Debye and Fermi temperatures are listed in the table below:

Table I. Typical Debye and Fermi Temperatures [5-6]

Element	Debye Temp (K)	Fermi Temp $\times 10^4$ (K)
Aluminum	428	13.6
Lead	105	11.0
Lithium	344	5.51
Iron	470	13.0
Potassium	91	2.46
Calcium	230	5.43
Carbon	2230	N/A

IV. CRYOGENIC AND ELECTRONIC SETUP

The first step of this project is to set up the equipment. I used a setup that has cryogenic (low-temperature portion) and electronic parts. For this project I used a calorimeter, thermometers for a sample platform and thermal reservoir (so-called block), heaters for the platform and block, and a lock-in amplifier for the Wheatstone bridge circuit. The calorimeter includes a long evacuated tube leading to the platform and block and is inserted into a bath of liquid helium to last the entire experiment. The block holds the leads to the circuit. These leads are soldered to silver pins embedded in the block for

thermal contact [7]. All electronics are controlled by a LabVIEW² program on a computer.

A. Wheatstone Bridge

During this experiment, I used the Wheatstone bridge circuit for the thermometer on the sample platform. See Figure 2.

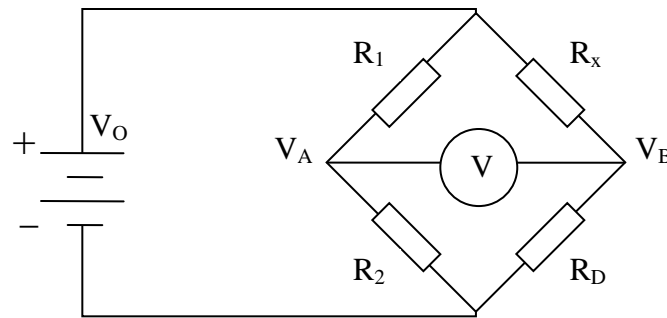


Fig. 1 Wheatstone bridge circuit [8].

The Wheatstone bridge was invented by Samuel Hunter Christie in 1833. In 1843 Sir Charles Wheatstone popularized the bridge (hence the name). It is an instrument that measures unknown electrical resistance. It contains two balanced legs and one leg that holds the unknown resistance. If the ratio of the two known legs is equal to the ratio of the variable leg (R_D) and unknown leg (R_x), then the voltage across the voltmeter should be zero (V_A to V_B). With this in mind we can set the variable resistance until there is no voltage across the voltmeter.

In my experiment setup, R_D is a decade resistor. R_1 and R_2 are 1 k Ω metal-film resistors, and R_x is the resistance of the platform thermometer, the unknown resistance to be found using the decade resistor. For V_o , I use the reference output of the lock-in

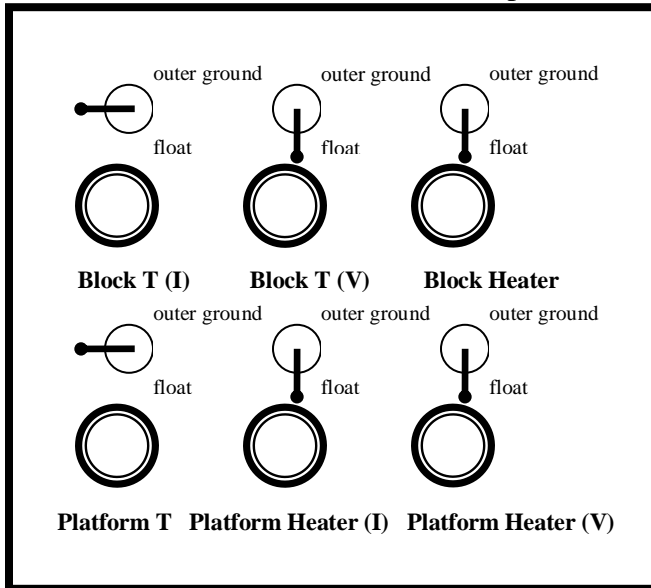
² National Instruments, 11500 N Mopac Expwy, Austin, TX, 1986.

amplifier set at 880 Hz, instead of a DC voltage source as shown in Fig. 1, and the lock-in amplifier for V .

B. Cryogenic Setup

The cryogenic setup includes the top-loading probe and attached calorimeter in a bath of liquid helium. The electrical leads from the calorimeter are connected to the breakout box (shown in Fig. 2), from which cables run to the current sources, voltmeter, and the Wheatstone bridge.

The calorimeter I used for this experiment is described in detail by H. Tsujii, *et al.*



[7]. This calorimeter is housed in a brass can. The can serves to thermally isolate the calorimeter from the surrounding temperature of the liquid helium. The leads that flow into the calorimeter are connected to 12 pins, which are

embedded in the block to thermalize the leads. The block is a 6.3 mm-thick silver block that is attached to the lid of the vacuum can [7]. Measuring the specific heat using the relaxation method and a non-digital lock-in amplifier, though slightly tedious, produces highly reliable results when methods are applied correctly. The relaxation method involves heating a sample to a specified temperature, turning off the heat, and monitoring the exponential curve of the

sample temperature as it relaxes to its original value. This data, examined over many different temperatures, will provide the specific heat equation.

V. PROCEDURE

My project has the following procedures. First, I set up the equipment (Wheatstone bridge circuit and computer). Then, after checking the probe for leaks, I inserted the probe and attached calorimeter into a dewer of liquid helium. Once the probe is cooled to 4.2 K, data is taken at temperatures from 5-16 K. After all data had been taken, I analyzed the data using Origin³. All good data must be cleaned, averaged, and fit. After this procedure the final results were compared to those of other published works and authors.

A. Preparing the Calorimeter

In order to prepare the top-loading probe and attached calorimeter for the experiment, I completed many steps. First, I removed the probe from its wooden container. I then removed the tape (wrapped around the barrel to prevent injuries) from the barrel. While supporting the platform with a small plastic support, I wiped the platform clean using acetone. This procedure should only be done to the platform's top surface, on which the sample will be placed, not to the bottom surface on which the thermometer and heater strips are located. Once the platform became opaque in color, I added about 0.5 mg of Wakefield Compound 120⁴ to the platform, and added a 145.37

³ Microcal™ Origin™. Version 4.10 (Microcal Software, Inc., Northampton, MA, 01060)

⁴ Wakefield Thermal Solutions, 33 Bridge St., Pelham, NH 03076.

mg sample of platinum to the platform (making sure that the bottom side of the platinum was covered in grease).

B. Setting the Phase

The process of taking data is the most vital part of the procedure. I began by setting the phase and resistance correctly. To do this, I started with the lock-in amplifier as an AC voltmeter. I then found the decade-resistor value that minimized voltage detected. Next I switched the lock-in amplifier back to the phase-sensitive mode and adjusted the phase to make the voltage zero. I then increased the phase by 90° and varied the decade resistance by about 10% in either direction. I then further adjusted the phase. If the output meter did not move in either direction when the resistance was changed by about 10%, then the phase setting was correct. Next I decreased the phase back by 90° and again set the resistance so that the lock-in amplifier read zero. Once the resistance has been set properly, this number is inputted into the computer as Rpl_L (platform resistance low).

C. Setting the Platform Heater

My next step was to set the platform heater. I first found the present temperature of the platform. Then I inputted an estimated value for the platform heater that would give me the temperature I wanted to reach, waited for the temperature to become stable, and then allowed the computer to determine the final temperature. From this given temperature, I raised the platform temperature by about 3%.

D. Optimization of Excitation

The next step was to find the optimized excitation level. First I set the sensitivity of the lock-in amplifier to 2 μV . Then I decreased the decade resistance so that the lock-in amplifier read a slightly negative voltage. I then checked the excitation level by increasing it to the greatest possible excitation that does not heat the platform thermometer. A usual rule of thumb is that as the temperature increases the excitation must increase.

E. Taking the Data

The final step was to take the data. After the previous steps were carried out, I was ready to take data. The LabVIEW program takes data on command. It is vital to wait for the probe to relax back to its original temperature before taking another data point.

VI. DATA ANALYSIS

Once all of the data had been taken, I analyzed the data using data analysis software, Origin. The data analysis portion consisted of platform thermometer calibration and refitting the relaxation curve. Then these two portions were conjoined to produce the final result.

A. Platform Thermometer Calibration

I took the master file and extracted the block resistance, block temperature, and platform resistances. After using the block resistance to recalculate an accurate block

temperature, I plotted the low platform resistance against the block temperature. Then I fit this plot with Origin.

B. Refitting the Relaxation Curve

Now I edited the master file and printed it out to a Microsoft Word⁵ document. I used Origin to view the relaxation curves at each temperature and identify bad ones. Because of an electronic, periodic noise of 20 Hz, the a program finds this noise and subtracts it. I call this step “cleaning”. Then I averaged the clean curves and fit them using multiple C programs. After this step was completed for all temperatures, I combined the platform thermometer calibration and the clean relaxation curves.

C. Combining the Two

I combined the two previous steps by inputting the platform low and high resistances, block resistance, and tau. I used a previously written C program that outputs the specific heat at each temperature and modified it for my purposes. The program output data became the plots for the final graph. From this graph, I extracted the final equation. This equation is the specific heat of the substance and is in the form of Eq. (3). Once the specific heat equation was found, the Debye temperature (θ_D) could be extracted from the coefficient of the cubic term.

⁵ Microsoft Corporation, 1983.

VII. SPECIFIC HEAT RESULTS AND CONCLUSIONS

Table II lists our results from this experiment. We found our final Debye temperature to be 219.20 K with an uncertainty of ± 0.63 K. Our parameters for the specific heat equation compared to those of other published works are listed in Table II: .

Table II. Resulting parameters associated with specific heat [9-10].

	γ (mJ/K ² mol)	θ_D (K)
Oliver	8.00 ± 0.96	219.20 ± 0.63
Martin	6.49 ± 0.01	238.70 ± 0.70
Gleeson <i>et al.</i>	6.50 ± 0.02	239.70 ± 1.10

Figure 3 provides a visual demonstration of the differences in my results and those of previous published works.

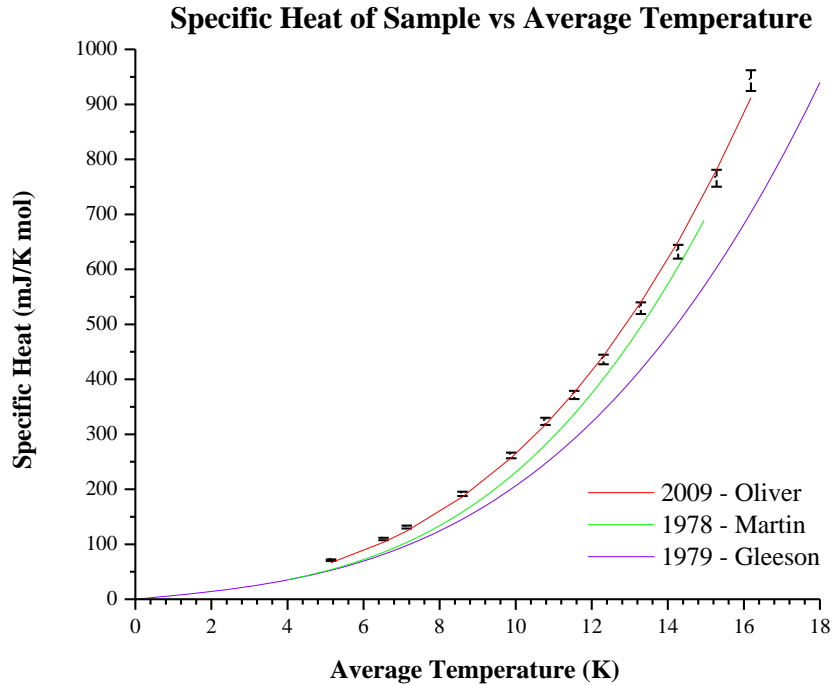


Fig. 3. Specific heat of platinum at temperatures below 16 K.

I have concluded that my Debye temperature is off from those of other published works because the probe was last calibrated in 2001. This fact most likely affected the thermal conductance of the probe and therefore directly altered the specific heat. I have also taken the platinum purity into consideration. The metal basis is 99.997%, an impurity level of 30 ppm. This level may have changed the property of the conduction electrons, causing an error in the specific heat results.

VIII. ACKNOWLEDGMENTS

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