



Heat Capacity of Vanadium Oxide (Heat Capacity Option)

<http://education.qdusa.com/experiments.html>

Prof. Richard Averitt¹ and Prof. Stephen Tsui²

¹University of California, San Diego

²California State University San Marcos

Description: The objective of this educational module is to measure the heat capacity of vanadium dioxide (VO_2), a material that exhibits a structural phase transition at 340K that coincides with a transition from a low-temperature monoclinic insulating phase to a high temperature rutile metallic phase [1]. VO_2 is a well-known correlated electron material that is being actively investigated to elucidate the relative importance of structural changes versus electronic correlations as the fundamental cause of the transition. The insulator-to-metal transition in VO_2 is first order resulting in a large latent heat, which can be measured using the heat capacity option of the VersaLab.

Preliminary Questions and Warm-Up:

- Define heat capacity.
- What is the relationship between heat capacity and temperature?
- When a substance, such as water, undergoes a phase transition, what happens to the temperature of the substance?
- If you were to plot the heat capacity vs. temperature for a first order phase transition, what might you expect from the data?

The metal-insulator transition in vanadium dioxide (VO_2) is depicted in Figure 1. You may find it surprising that heating up this black ceramic material past the boiling point of water will cause its resistivity to drop several orders of magnitude! Hence, we call this phenomenon a metal-insulator transition. Imagine what you could engineer with a material that can change electrical behavior as it crosses a certain temperature threshold. What might be some uses of this?

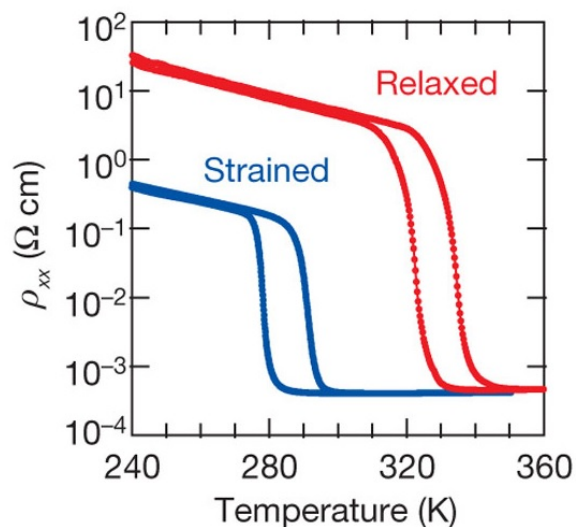


Figure 1. The metal-insulator transition for VO₂ [2].

In order to perform an electrical resistance characterization, one typically attaches four wires to a material. VO₂ is fairly powdery, so observing the metal-insulator transition using wires will not work very well. Here is your chance to use another method to explore this transition: a heat capacity measurement.

Objectives:

- Prepare the VersaLab to measure heat capacity.
- Run an addendum measurement to calibrate the heat capacity measurement system.
- Measure the heat capacity of VO₂ near the phase transition.
- Identify features in the heat capacity that correspond to the latent heat of the phase transition.

Student Learning Outcomes:

- Students will gain experience with small sample handling.
- Students will learn how to perform a heat capacity measurement.
- Students will observe a first order phase transition and experience the technical nuances with such a measurement.

Safety Information:

Before attempting to perform any parts of this student experiment, please read the entire contents of: this Educational Module, the VersaLab User's Manual (1300-001), and Heat Capacity Manual (1085-150), and observe all instructions, warnings and cautions. These are provided to help you understand how to safely and properly use the equipment, perform the experiments and reach the best student learning outcomes.

Quantum Design Inc. disclaims any liability for damage to the system or injury resulting from misuse, improper operation of the system and the information contained in this Educational Module.

The following Safety warnings apply to this Educational Module. We recommend that you study them carefully and discuss the details with your instructor before starting the work:


WARNING!

Always use **Personal Protective Equipment (PPE)** during every step of sample preparation. Failure to do so might cause bodily harm.




TOXIC HAZARD!

Vanadium Oxide (VO_2) is hazardous in case of skin contact (irritant), or eye contact (irritant). For more information consult the Material Safety Data Sheet available on this website:
<http://www.guidechem.com/msds/12036-21-4.html>




CRUSHING HAZARD!

Before using the die and hydraulic press, please read the entire contents of the User's Manual specific to that equipment, and observe all instructions, warnings and cautions. Failure to do so might cause bodily harm.



HOT SURFACE!

Before using the furnace and combustion boats to sinter the samples, please read the entire contents of the User's Manual specific to that equipment, and observe all instructions, warnings and cautions. Failure to properly handle hot surfaces might cause bodily harm.



FIRE HAZARD!



Before using the furnace to sinter the samples, please read the entire contents of the User's Manual specific to that equipment, and observe all instructions, warnings and cautions. Failure to do so might cause a fire hazard, bodily harm.

Experimental Instructions:

In this section, we provide guidance on preparing and measuring the heat capacity of VO_2 . Our focus will be on observing the first order phase transition occurring at $\sim 340\text{K}$. As such we will utilize the slope analysis of relaxation curves to obtain the data.

Several items are needed for this experiment, which includes:

- *Apiezon H grease. Importantly, the specific heat of N grease is strongly temperature dependent above 200K, so H grease is recommended to minimize errors.*
- *Grease applicator which can be the wooden end of a cotton swab*
- *A microscope to facilitate the application of the grease and sample*
- *A precision scale with 0.1 mg or better resolution.*
- *Weigh boats or wax paper for handling the VO_2 .*

a.) Prior to preparing for the sample measurement, the heat capacity module should be installed and activated. In addition, make certain that the vacuum chuck and pump that are part of the heat capacity option are in an easy to access location.

b.) Locate the heat capacity puck and thermal radiation shield.

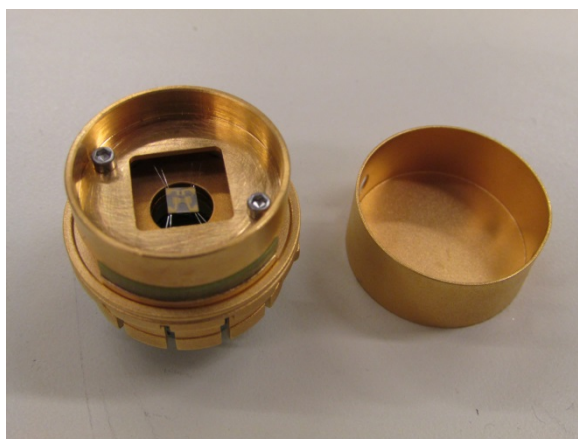


Figure 2: Heat capacity puck and shield

- c.) Verify that the serial number of the puck is consistent with the calibration file that in MultiVu. This can be checked in the heat capacity control center (see section 4.4. of the user manual). Click on the “files” tab will enable identification of the calibration file. In the following, we will assume that the puck in use has been properly calibrated. If not, the procedure in Chapter 5 of the heat capacity user’s manual must be followed.
- d.) The next step is to prepare the puck for the addenda measurement. This requires placing H grease on the puck. For this, the vacuum chuck and pump are needed. This is to stabilize the puck while working with it, since the sample platform is very fragile and it is easy to break the wires! Figure 5 shows the chuck with the heat capacity puck inserted. With the silver arm in the open position as shown, the vacuum is not on. Upon closing (see Fig. 8) the vacuum line will be activated (make sure the pump is on!) which will gently pull the sample platform into place, thereby stabilizing it for grease application.

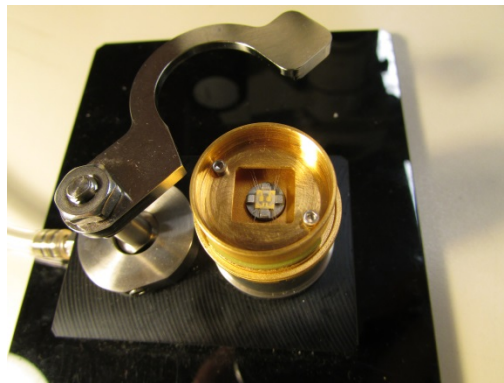


Figure 3: Heat capacity puck on vacuum chuck.

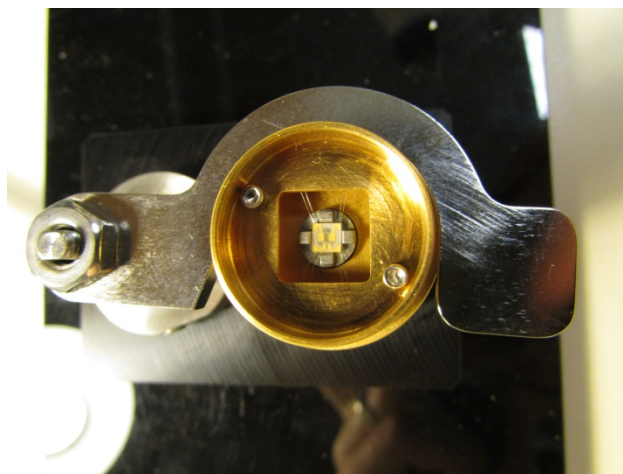


Figure 4: With the silver lever closed the platform is stabilized.

e.) The next step is to place the H grease on the platform, being careful to not touch the wires. There are two reasons for this. First, the wires could break. Secondly, any grease that gets on the wires will change the thermal conductance, which could invalidate the calibration. Figure 5 shows the grease being placed on the sample stage, and Figure 6 shows a close up of the sample stage after the grease application.

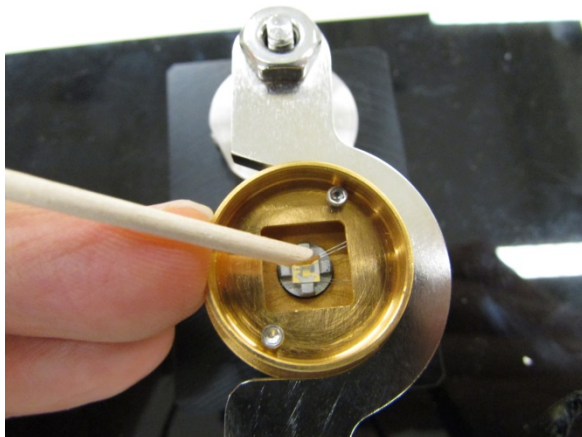


Figure 5: H grease application to sample platform

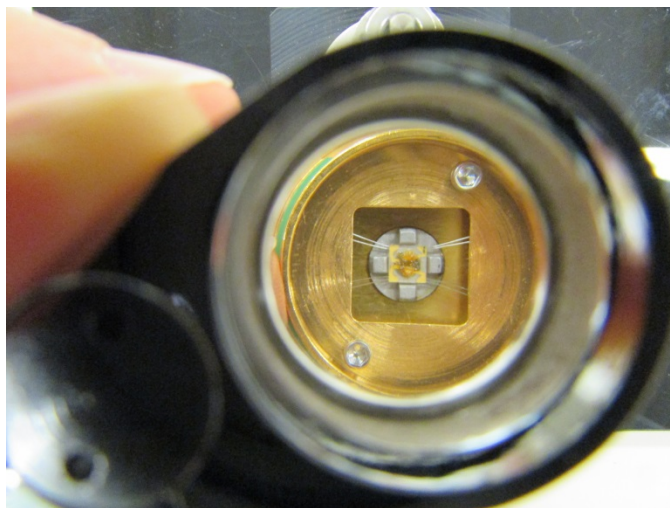


Figure 6: Sample platform with grease applied.

f.) The next step is to perform the addenda measurement. First, ensure the thermal radiation shield is firmly fastened to the puck as shown in Figure 7.

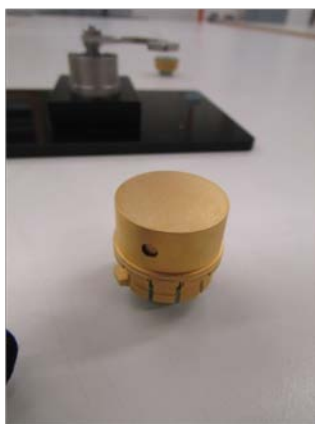


Figure 7: Heat capacity puck ready for addenda measurement

g.) The puck can now be loaded into the VersaLab (Figure 8), and the VersaLab chamber sealed using the cap with the vacuum bellows (Figure 9).

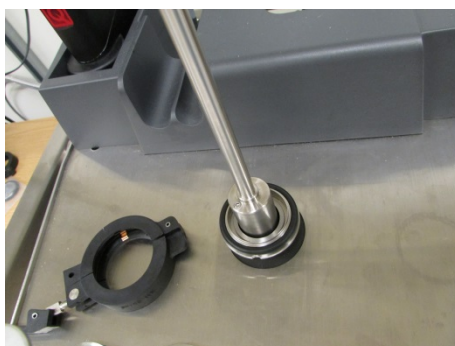


Figure 8: Loading the puck into the VersaLab.



Figure 9: Sealing the VersaLab for the addenda measurement

h.) In the heat capacity control center (again, see section 4.4 of the users manual), the addenda measurement can easily be performed. Under the measurement tab, there is the option to create a new addenda table. The temperature range can be selected. For these measurements, we are interested in the temperature range from approximately 325K – 350K which extends well below and above the transition temperature in VO₂. For the addenda measurement choose 290K – 370K to be certain that the range of interest is covered. The addenda measurement will take some time (potentially overnight) and will create an addition to the calibration file that will be used for the subsequent sample measurements.

Sample Preparation:

While the addenda is running, you can now prepare your sample. VO₂ is a skin and eye irritant and must be handled with care. Use proper personal protective equipment (gloves, mask, eyewear). The safety datasheet (MSDS) for VO₂ can be found online here: <http://www.guidechem.com/msds/12036-21-4.html>

Although it is possible to perform this experiment using powder, a more reliable measurement can be obtained by pressing the powder into a pellet using a die and hydraulic press.

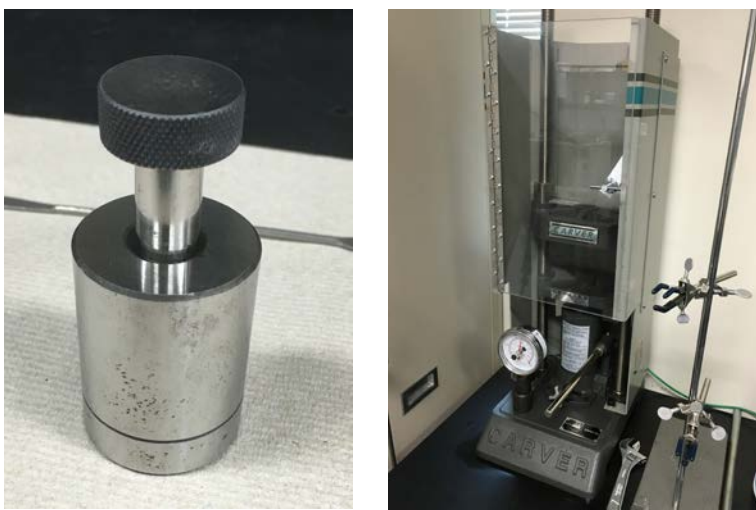


Figure 10. 13 mm die set (left) and hydraulic press (right).

Fill a small amount of powder into the die. Applying 13,000 pounds of with the hydraulic press is sufficient to yield a pellet. It is likely to be a fairly soft and fragile sample, and you may choose to sinter the pellet at 200° Celsius for one hour to improve the structural quality.

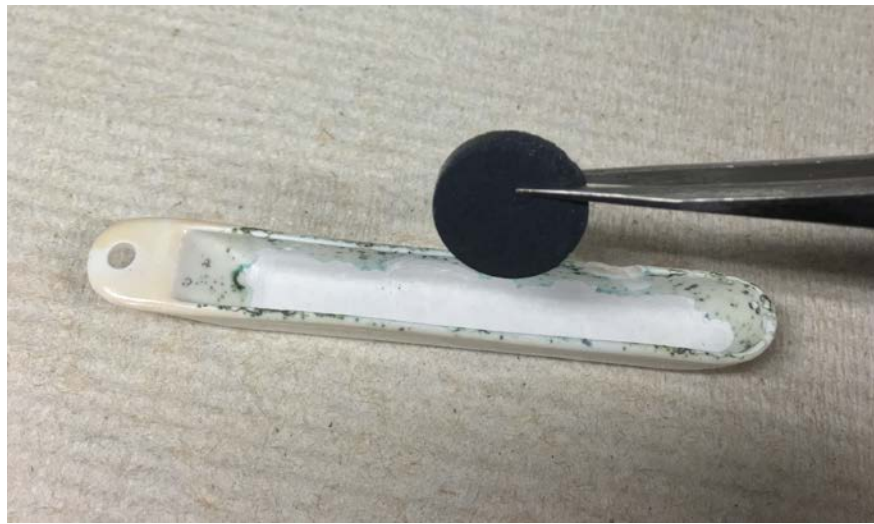


Figure 11. Pressed VO₂ pellet.

It should be fairly easy to break off a small piece of sample by poking at it with a stick or tweezers in order to fit into the heat capacity puck. Do this after the addenda measurement is complete.

Returning to the Instrument:

- i.) After the addenda measurement is completed and the sample puck is at room temperature, it can be removed from the VersaLab in preparation for placing the sample onto the heat capacity platform.
- j.) The first step is to break off a piece of your sample and weigh it. Only a few mg are needed, so small, thin pieces are preferred to make sure there is good coupling with the measurement platform. Note that the platform is 3x3mm so pieces must be smaller than this.
- k.) The heat capacity puck should be placed back in the vacuum chuck for the mounting of the sample. You may find it useful to have the puck under the microscope.
- l.) The sample should be gently placed onto the platform in the area where the H grease is located. It is important to not remove any grease as this will invalidate the previously obtained addenda.

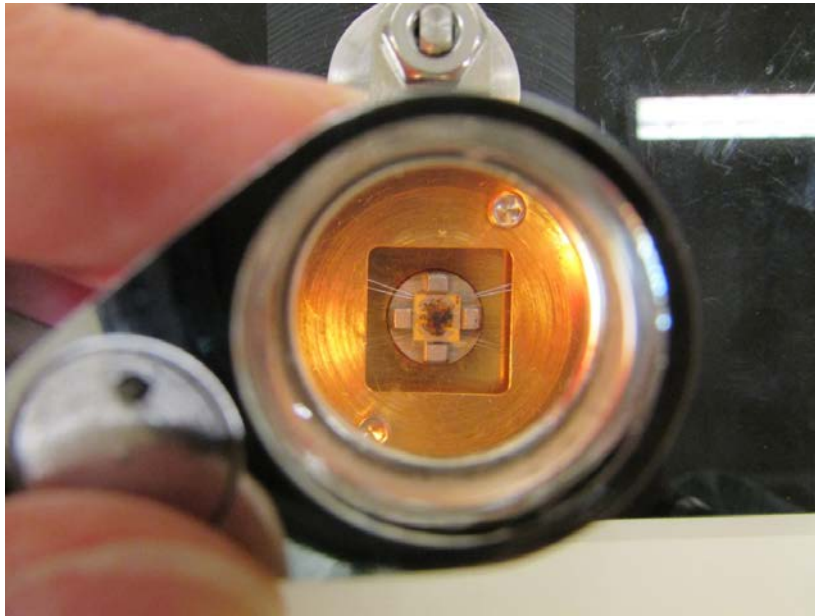


Figure 12: Heat capacity puck with VO₂ deposited.

- m.) Remove the heat capacity puck from the vacuum chuck, seal it with the thermal shield (i.e. as in Figure 7) and place it in the VersaLab to prepare for the heat capacity measurement.
- n.) After the sample is loaded, you are ready to perform the heat capacity measurement. In the heat capacity control center, it is possible to initiate a measurement. We will write a simple sequence that will focus on measuring the heat capacity at 300 K, away from the transition.

Set Temperature 300K at 12K/min. Fast Settle
Wait For Temperature, Delay 0 secs, No Action
Sample HC at current temperature, 2% rise, 3 times, 2 tau meas time
Set Temperature 300K at 12K/min. Fast Settle

- o.) The real-time measurement status viewer should appear when the measurement starts. Alternatively, on the Files tab, you can click on Meas Status in order to bring it up. As the measurement progresses, you can expect the display to be similar to that shown in Figure 13.

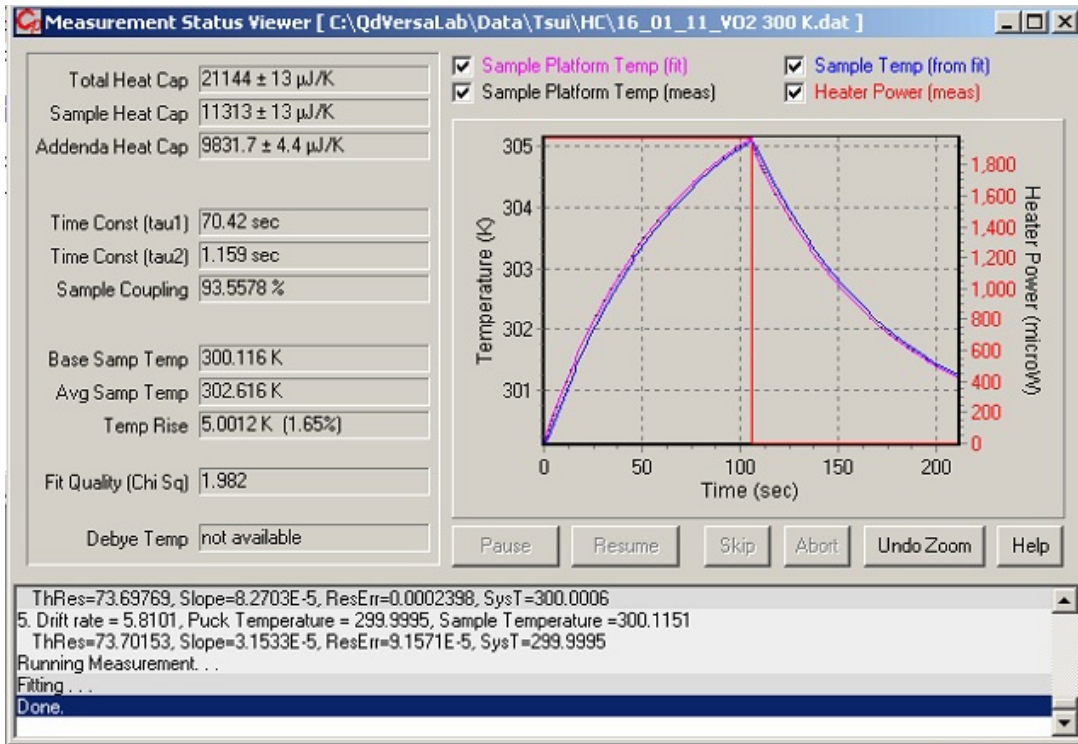


Figure 13. Measurement Status Viewer.

p.) On the left of Figure 13 you see the Heat Capacity software has analyzed the curves on the right to obtain a single value for the heat capacity, which is its normal mode of operation. However, the data can be further analyzed using MultiVu. From the heat capacity control panel (Figure 14, left side) under tab Files, select "Raw Data File Viewing and Post Processing." A screen will appear as in Figure 14 on the right.

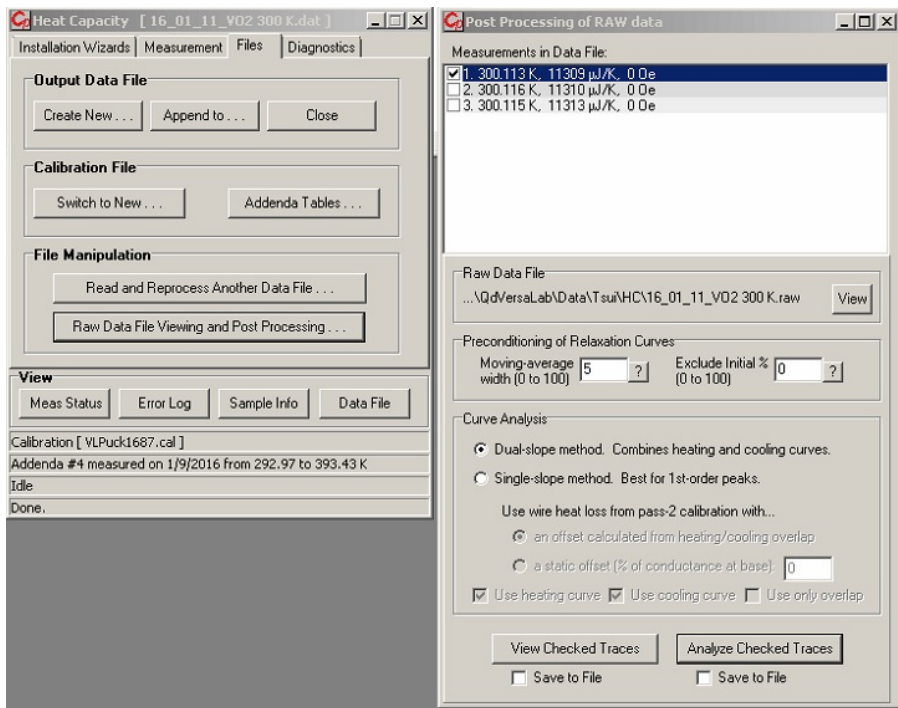


Figure 14. Screenshot of control panel and post-processing window.

- q.) Select the dual-slope curve analysis method. You can then view the checked traces (of which there are three as performed from our sequence), which will bring up a window of the raw data, which replicates the status in Figure 15. Save this data to a file.
- r.) Alternatively, one can select to analyze the checked traces. The data will be analyzed and plotted. The plot shows the experimentally obtained heat capacity in $\mu\text{J}/\text{K}$. Save this data to a file.
- s.) Now, we will examine the transition and write a simple sequence that will focus on measuring the heat capacity over the temperature range from 325 to 350K, appropriate for measuring the first order phase transition in the VO_2 powder. Here is a sample sequence to accomplish this:

Set Temperature 325K at 12K/min. Fast Settle
 Wait For Temperature, Delay 0 secs, No Action
 Sample HC at current temperature, 25 K rise, 3 times, 3 tau meas time
 Set Temperature 300K at 12K/min. Fast Settle

This sequence sets the initial temperature to 325K, then performs a measurement three times, ramping the temperature up to 350K. Once the sequence is initiated, the measurement status viewer will appear on the screen to enable tracking of the measurement. You may obtain a warning about inaccurate C_p values arising from this sequence. This warning is given since a large temperature range is being covered which

would lead to errors in a conventional fitting with a 1-tau or 2-tau model. However for the slope analysis method, a sufficient temperature rise covering the first order phase transition is what we want.

- t.) The data can be analyzed using MultiVu. From the heat capacity control panel (Figure 15, left side) under tab Files, select "Raw Data File Viewing and Post Processing." A screen will appear as in Figure 15 on the right.

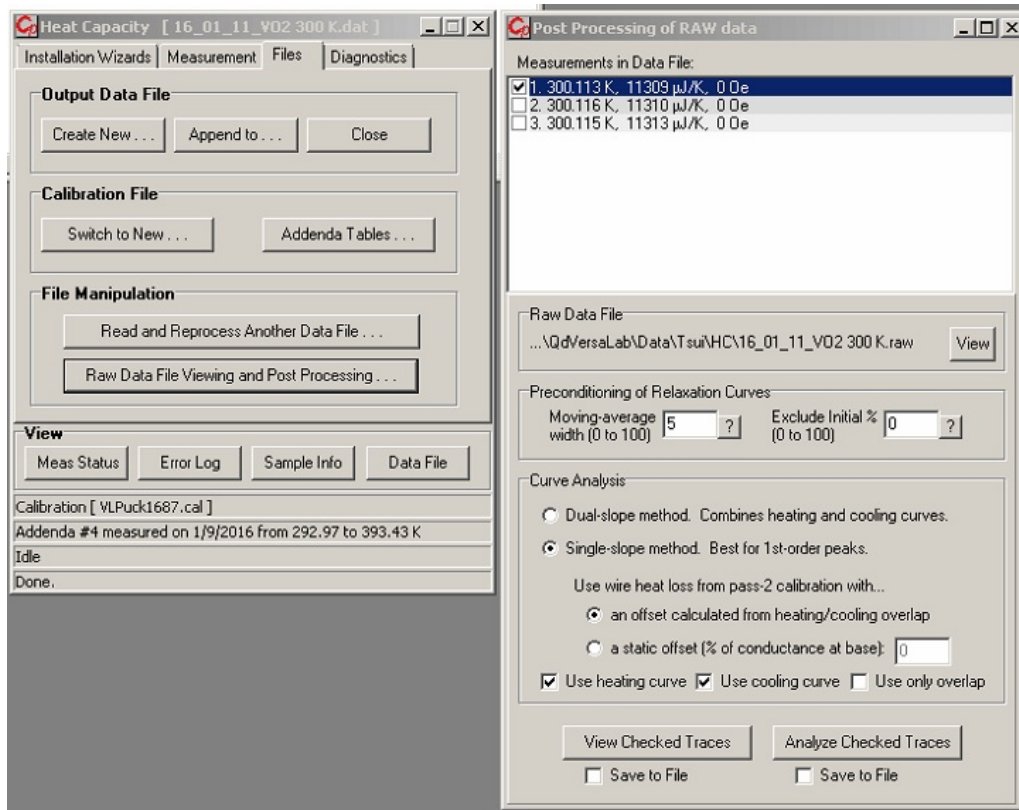


Figure 15: Screenshot of control panel and post processing window

- u.) Select the single slope curve analysis method appropriate for a first order phase transition. You can then view the checked traces (of which there are three as performed from our sequence), which will bring up a window of the raw data. Save this data to a file.
- v.) Now analyze the checked traces. Save this data to a file.

Questions / Analysis:

1. How does the data differ at temperatures away from the transition and at the transition? What do you notice in both the raw data and the checked traces?

- Analyze your data to estimate the mass specific heat below the phase temperature. Provide an estimate of the error bars and compare your result to experimentally published data for crystals.
- Now analyze your data to obtain an estimate of the latent heat. Again, provide error bars, compare to literature values.

Note: for 1 and 2 you could use the data from C. N. Berglund, H. J. Guggenheim, Phys. Rev. **185**, 1022 (1969) for comparison. Or you can find other data in the literature if you so choose.

- Find a review paper on VO_2 , and write a paragraph summarizing the interesting properties of this material. Discuss how the heat capacity plays an important role in understanding the physics of this material.

Additional Background:

The heat capacity [J/K] characterizes the increase in the internal energy of a system for a given temperature increase. Considering the first law of thermodynamics we have $dU = dQ + dW$, where dU is the change in energy when either work (dW) is performed or heat (dQ) is added to the system. This expression can also be written as $dU = TdS - PdV$ where the notation follows standard conventions. The heat capacity is defined as $C = dQ/dT$ which, for constant volume, is $C_v = dU/dT = T(ds/dT)$ [3,4]. The heat capacity is extensive (i.e. it depends on the quantity of material). It is more useful to express it as an intensive quantity. Two common intensive descriptions are the mass heat capacity (often called the mass specific heat) with units J/(kg K) and the molar heat capacity (often called the molar specific heat) with units of J/(mol K). The same symbol c_v is typically used for either specific heat quantity, so care must be taken to specify the units. For solid-state measurements, it is usually the specific heat at constant pressure c_p that is measured. The connection between c_p and c_v is $c_p - c_v = 9\alpha^2VT/\kappa$ where α [1/K] is the linear coefficient of expansion, κ [ms²/kg] is the compressibility, and V [m³/kg] is the specific volume. We will not worry about this distinction in what follows.

Heat capacity measurements provide fundamental insight into the properties of a material. As you may recall, the classical result of Dulong-Petit for the molar heat capacity of a solid is $c = 3R = 24.9$ J/(mol K) where $R = 8.31$ J/(mol K) is the ideal gas constant. This provides reasonable agreement with the room temperature measurement of many solids (e.g. Aluminum (24.2), Fe (25.1)). However, strong deviations of materials such as diamond (6.1) and, more importantly, the temperature dependence of the heat capacity necessitated the use of quantum mechanics to obtain a more complete understanding. In Einstein's theory, the solid is treated as a harmonic oscillator with a single characteristic vibrational frequency ω [5]. This approach was able to provide a basic understanding of the decrease in the heat capacity with temperature. The data for diamond with Einstein's fit is shown in Fig. 1. In this plot the units are

cal/(mol K) which can be converted to J/(mol K) by multiplying by 4.184 J/cal. For diamond, the Einstein temperature is given by $T_E = \hbar\omega/k_B = 1320\text{K}$ indicating the approximate temperature at which the heat capacity reaches the classical Dulong-Petit value. The deviations at low temperature between experiment and theory in Fig. 1 is real, and a better fit is obtained with the Debye model which essentially quantizes sound waves. Amongst other things, the Debye model correctly predicts the T^3 dependence of the heat capacity [4].

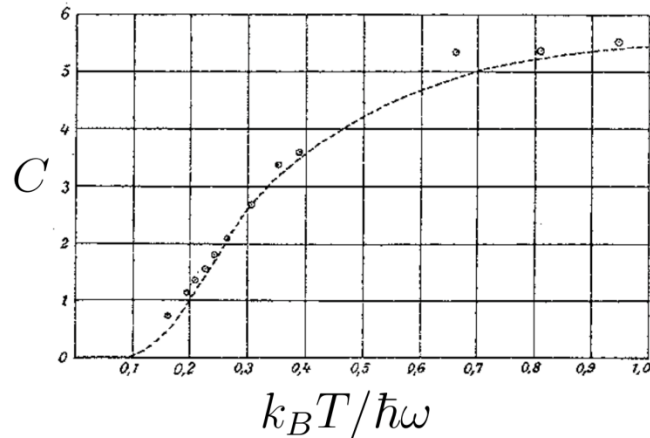


Figure 16: Comparison of Einstein model (dashed line) to experiment (circles) for the molar specific heat of diamond from [5].

Importantly, other degrees of freedom in solids also have a heat capacity. For example, in metals the specific heat exhibits a linear dependence on temperature $c = \gamma T$ arising from the free electrons (γ is the Sommerfeld coefficient). This was first correctly obtained in free electron (or Sommerfeld) theory using Fermi-Dirac statistics for the electrons [4]. Of course, $c = \gamma T$ is just for the electrons, and the lattice must also be included. At low temperatures, $c \approx \gamma T + \beta T^3$ where the first term is for the electrons and the second term the lattice. At high temperatures the lattice will dominate, but the electron contribution becomes important in metals at low temperatures.

In contemporary condensed matter physics, the fact that heat capacity measurements reveal interactions between various degrees of freedom is extremely important. As one example, we consider heavy-Fermion (HF) materials. As the name implies, in these materials (below a cross-over temperature), the electrons (really quasiparticles – i.e. dressed electrons) become extremely heavy. In some HF materials the quasiparticles exhibit an effective mass approaching 1000 times the mass of a free electron! This arises from interactions of the conduction electrons with localized f-moments in these materials. Importantly, the onset of HF phenomena appears in heat capacity measurements. This is because the heat capacity is proportional to the density of states at the Fermi level, which in turn is related to the effective mass [6,7].

Heavy Fermions are but one (fairly exotic) example. More generally, heat capacity measurements are sensitive to phase transitions. This includes magnetic

ordering, structural transitions, ferroelectric polarization, and superconductivity. This applies to both first order and second order phase transitions. In the case of a first order transition, a discontinuity appears in the entropy which in turn leads to a divergence in the specific heat since $c_v = T(ds/dT)$. This singularity is the latent heat L [J/kg] and is the increase in the internal energy needed to drive the phase transition [8]. In this module, the goal is to measure L for a VO_2 sample.

In the case of a second order (or continuous) phase transition, a kink appears in the entropy S , leading to a discontinuity in the specific heat. The importance of this can be understood from considering thermodynamic potentials. For example, for the Helmholtz free energy we have $F = U - TS$. From this we can see that the entropy is the driving "force" for a phase transition. At low temperature (below the phase transition temperature T_c), the entropy is not too important, and F can be minimized by having U minimized. This leads to ordering (e.g. of spins in a magnet). However, with increasing temperature the entropy becomes increasingly important, and minimizing F benefits from increased S corresponding to increasing disorder. In fact, the total entropy associated with the ordering can be determined from:

$$S = \int_0^{T_c} \frac{1}{T} c_p(T) dT \quad (\text{Eqn. 1})$$

In determining the entropy associated with ordering, it is important to exclude other contributions such as the lattice specific heat. An insightful description of second order (and also first order) phase transitions is Landau's mean field theory which provides a description in terms of an order parameter [8]. However, while providing considerable insight and a general framework for phase transitions, this theory does not include fluctuations, which affect the thermodynamic response and lead to interesting phenomena such as critical behavior in phase transitions [9,10]. A detailed description of critical phenomena, ordering and broken symmetry, etc., can be found in the references. Suffice to say, heat capacity measurements are a primary means to study these fundamentally important effects in solids.

The next question we must address is how are heat capacity measurements performed? The basic idea is to heat the sample in a precise manner to add a precise amount of energy and measure the corresponding temperature change. In the VersaLab heat capacity option, this is accomplished by applying a known amount of heat at constant power for a fixed amount of time followed by a cooling period while measuring the temperature as a function of time. This heating/cooling process is depicted in Figure 17. An appropriate model (discussed below and in Chapter 4 of the heat capacity user

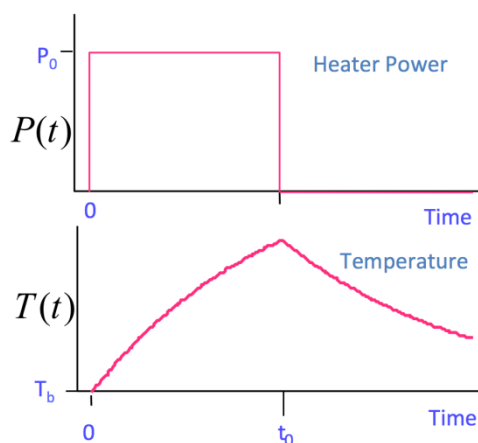


Figure 17: heat capacity measurement approach.

manual) is used to fit the time dependence of the temperature change which can be used to determine the heat capacity.

For accurate measurements, the heat capacity hardware must be designed to have a low thermal mass and appropriate thermal conductance and thermal isolation. Fig. 18a gives a schematic depiction of the hardware, while Fig. 18b is a picture of the heat capacity puck used for the VersaLab.

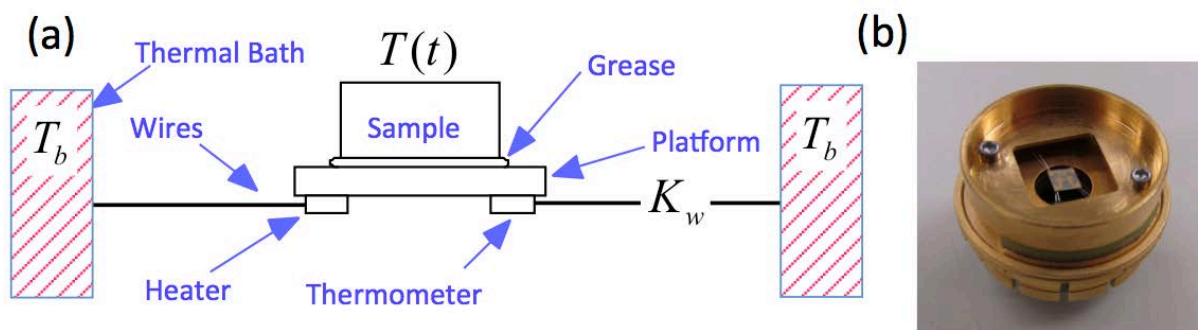


Figure 18: (a) Schematic of heat capacity hardware. (b) Heat capacity puck.

As shown in Fig. 18, a platform heater and platform thermometer are attached to the bottom side of the sample platform. Small wires provide the electrical connection to the platform heater and platform thermometer and also provide the thermal connection and structural support for the platform. The sample is mounted to the platform by using a thin layer of grease, which provides the required thermal contact to the platform.

The integrated vacuum system in the cryostat provides a sufficient vacuum so that the thermal conductance between the sample platform and the thermal bath (puck) is dominated by the conductance of the wires. This gives a reproducible heat link to the bath with a corresponding time constant large enough to allow both the platform and sample to achieve sufficient thermal equilibrium during the measurement.

The VersaLab measures heat capacity curves like that shown in Fig. 17 (i.e. the change in temperature versus time) and the data is fitted in MultiVu using one of several models. To give a feel for this, we describe the 1-tau model that fits the data using a single time constant. The details of the 2-tau model (which accurately takes into account the thermal conductance between the sample and the platform) are described in section 4.3 of the heat capacity user manual. The 1-tau model describes the flow of power into and out of the sample:

$$C_{total} \frac{dT(t)}{dt} = P(t) - K_w(T(t) - T_b) \quad (\text{Eqn. 2})$$

where C_{total} is the total heat capacity, $P(t)$ is the applied power, K_w is the thermal conductance of the wires, $T(t)$ is the time-dependent temperature, and T_b is the bath temperature. For $P(t)$ (see Fig. 17) we have $P(t) = P_0$ ($0 \leq t \leq t_0$) and $P(t) = 0$ ($t > t_0$). With the initial conditions, $T_{on}(0) = T_b$ and $T_{on}(t_0) = T_{off}(t_0)$, Eqn. 2 can be solved yielding:

$$T(t) = \begin{cases} \frac{P_0 \tau \left(1 - e^{-\frac{t}{\tau}}\right)}{C_{total}} + T_b & (0 \leq t \leq t_0) \\ \frac{P_0 \tau \left(1 - e^{-\frac{t}{\tau}}\right) e^{-(t-t_0)/\tau}}{C_{total}} + T_b & (0 > t_0) \end{cases} \quad (\text{Eqn. 3})$$

where $\tau = C_{total}/K_w$ is the thermal time constant. MultiVu uses least squares to obtain a best fit for the heat capacity. Performing these thermal time constant measurements at a series of temperatures allows for the determination of the heat capacity as a function of temperature.

It is important to note that C_{total} is the total heat capacity of the sample platform, the grease, and the sample of interest. Thus, several measurements are actually required to obtain C_p of the sample. First, the puck must be calibrated. That is, a measurement must be performed without the grease or the sample. This procedure needs to be performed for each new puck to determine the heat capacity of the sample platform and K_w . The data for this calibration is saved in a ".cal" file for reference with the subsequent measurements. For each new sample to be measured, an addenda must first be obtained. This is essentially a measurement of the heat capacity of the grease and the sample platform **without** the sample. This is also saved in the calibration file. Finally, the sample/grease/sample platform heat capacity is measured. From this series of three measurements, it is possible to obtain C_p of the sample of interest.

While this approach for measuring the heat capacity enables measurements over a wide temperature range, it could easily miss features in the specific heat associated with first or second order phase transitions if, for example, the selected number of temperatures is too sparse. This is because the heat capacity associated with phase transitions can be quite narrow (this is particularly true for first order transitions). Thus, an alternative approach to measure (or search

for) the phase transition must be utilized.

In our study of VO₂, we will utilize the slope analysis method of relaxation curves. If both sides of Eqn. 2 are divided by $dT(t)/dt$, one obtains:

$$C_{total} = \frac{P(t) - K_w(T(t) - T_b)}{dT/dt} \quad (\text{Eqn. 4})$$

This provides an operational approach to obtain the heat capacity as a function of temperature from a single curve such as that shown in Fig. 17. At each time, the slope is calculated, thereby providing a means to obtain C_{total} at each temperature on the curve! In the case of a first order phase transition, there should be a distinct decrease in the slope at the transition temperature. This intuitively makes sense since the latent heat requires the addition of energy to the sample without a temperature increase. Further, since first order transitions exhibit hysteresis, the warming and cooling curves will have different kinks in the slopes. Section 4.3 of the heat capacity user manual presents additional details while section 4.6 provides examples of single slope analysis of a first order phase transition in Figures 4-6 and 4-7. It is strongly advised that chapters 1-4 of the heat capacity users manual is read prior to performing these measurements.

Notes:

1. F. J. Morin, Phys. Rev. Lett. **3**, 34 (1959); see also C. N. Berglund, H. J. Guggenheim, Phys. Rev. **185**, 1022 (1969); N. Mott, *Metal-Insulator Transitions*, Taylor and Francis, London, 1977.
2. M. Nakano et al., *Nature* 487, 459 (2012).
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4. Steven H. Simon, *The Oxford Solid State Basics*, Oxford University Press, Oxford, 2013.
5. A. Einstein, Ann. Phys. 22, 180 (1907); see also any solid state physics book such as Simon's book in reference three.
6. http://en.wikipedia.org/wiki/Heavy_fermion
7. P. Coleman, Heavy Fermions: Electrons at the edge of magnetism, <http://arxiv.org/abs/cond-mat/0612006v3>
8. David L. Sidebottom, *Fundamentals of Condensed Matter and Crystalline Physics*, Cambridge University Press, Cambridge, 2012. Chapter 15.