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FY04 LDRD Final Report Small Sample
Heat Capacity Under High Pressure
LDRD Project Tracking Code: 04-FS-020

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February 15, 2005

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This work was performed under the auspices of the U.S. Department of Energy by University of California, Lawrence Livermore National Laboratory under Contract W-7405-Eng-48.

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Abstract

Specific heat provides a probe of bulk thermodynamic properties, including low energy excitations (phonons, magnons, etc), the electron density of states, and direct observation of phase transitions. The ability to measure specific heat as a function of pressure permits study of these properties as a function of lattice parameters. This in turn should allow construction of an equation of state for a given system. Previous measurements of specific heat under pressure done by adiabatic methods were limited to materials with extremely large heat capacities because it was difficult to decouple the sample heat capacity from the surrounding pressure cell. Starting in the late Seventies, Eichler and Gey[1] demonstrated an AC technique to measure heat capacity of relatively small samples (~ 100 's mg) in a piston pressure cylinder at pressures up to 2 GPa. More recently, this technique has been expanded to include work on significantly smaller samples (< 1 mg) in large diamond anvil cells (DAC)[2]. However, these techniques require a relatively weak coupling of the sample to the surrounding thermal bath, which limits the base temperature, particularly for radioactive samples possessing significant self-heating such as plutonium. A different technique, sometimes referred to as the 3ω -technique, utilizes a two dimensional heat flow model to extract heat capacity, C , and κ , the thermal conductivity, from an oscillating heat input. One advantage of this method is that it does not require that the sample be thermally isolated from the heat bath, so lower base temperatures should be accessible to interesting self-heating samples. From an experimental perspective, the design requirements of the 3ω and AC techniques are quite similar. We focused on development of these techniques for a copper-beryllium (CuBe) pressure clamp for use on small samples at temperatures down to 1.7K and at pressures up to 1.6 GPa. The successful development of this capability will enable a new class of important physical property measurements on a variety of advanced and special materials, including plutonium.

Introduction/Background

Measurement of heat capacity is a direct probe of the entropy in a system, and thus provides a window to investigate the basic thermodynamic properties from which such information as the equation of state can be obtained. The most common technique, currently in use for measuring the heat capacity of small samples, is the quasi-adiabatic method. In this technique the sample is thermally isolated from the surrounding heat bath apart from a weak thermal link, effectively creating a thermal RC circuit. A heat pulse is then applied to the sample, and the temperature change of the sample is recorded as a function of time from which the value of the heat capacity may be extracted. This is a powerful technique that has found use across a wide range of temperatures and magnetic fields. Extending the technique to varying pressure would be an important advance, but it requires thermal isolation with a typical vacuum better than 10^{-5} mbar. Therefore, in order to investigate the heat capacity of advanced systems, such as samples under pressure or radioactive samples at low temperatures, where self heating in combination with a weak thermal link limits the obtainable base temperature, a new technique is required.

A method known in the literature as the 3ω -technique, has the potential to permit measurement of small samples under more extreme conditions of pressure and self-heating. It is a dynamic measurement, and actually requires a heat sink, so in some respects it is ideal for these types of measurements. The core idea exploits the temperature dependence of resistivity in pure metals. An AC current of frequency ω is applied to a metal strip, which in turn acts as both the heater and thermometer for the sample. This strip in turn heats at a frequency of 2ω , which is reflected in a change in resistance of the heater:

$$R(T) = R_0 + \alpha T \sim R_0 + \alpha(T_0 e^{2i\omega t}) \quad (1)$$

Where α is the slope of the resistance as a function of temperature for the heater/thermometer. Thus the overall signal observed then becomes:

$$V(t) = IR(T) = I_0 R_0 e^{i\omega t} + C\alpha I_0 T_0 e^{3i\omega t} \quad (2)$$

Here C includes a number of terms dependant on the geometry of the sample, boundary conditions, heater shape, etc. These may be obtained by solving the general dynamic heat transfer equation [5]:

$$\rho C_p \frac{\partial T}{\partial t} = -K \nabla^2 T \quad (3)$$

where ρC_p is the specific heat per unit volume, and K is the thermal conductivity. Solutions to this equation for a host of boundary conditions are available in the literature, and for the purposes of this work we are primarily interested in the solution to the 2 dimensional heat flow problem, which describes the heat flow from a wire into its surrounding environs. The solution can be approximated by the following equation:

$$V(t) = I_0 R_0 \left(e^{i\omega t} + a \frac{I_0^2 R_0}{\rho K l} \left[\frac{1}{2} \ln\left(\frac{D}{2wr^2}\right) + \ln 2 - 0.5772 - i \frac{D}{4} \right] e^{3i\omega t} \right) \quad (4)$$

Here K is the thermal conductivity of the sample, r is the wire thickness, l is the wire length, and D is the thermal diffusivity, given by: $D = K/\rho C$. Typically the third harmonic is about 10^4 times smaller than the fundamental, so the ability to measure this term is the key to success in the project. The thermal diffusivity is also related to the thermal penetration depth:

$$d_k = \sqrt{\frac{2D}{\omega}} \quad (5)$$

Which defines a characteristic length scale for which equation (4) is applicable. For the sample sizes of interest in this project, typically a few millimeters, a thermal penetration depth in the range of 0.1-1 mm was desirable, which typically corresponded to a frequency range of ~ 10 -1000 Hz.

Our plan, intended for pursuit over the course of a year, was to develop the ability to measure a small sample using the technique, repeat the measurement in a copper beryllium pressure cell at ambient pressure, and finally to complete the measurement under modest pressure.

Research Activities

Our research activities can be neatly divided into two parts: development of the 3ω measurement technique and design of the pressure clamp, which will be discussed in order below. We spent \$48k over five months, mostly to cover our time.

The 3ω technique

The instrumentation required included a function generator or current calibrator to provide the AC excitation current, a lock-in amplifier, and cryostat for temperature control. Most of the required instruments were readily available on site, including an SRS-850 Lock-In Amplifier, which has the ability to measure harmonics as well as the fundamental frequency. This greatly simplifies the instrumentation, as a frequency tripler need not be built. A simplified block diagram of the measuring circuit is shown below:

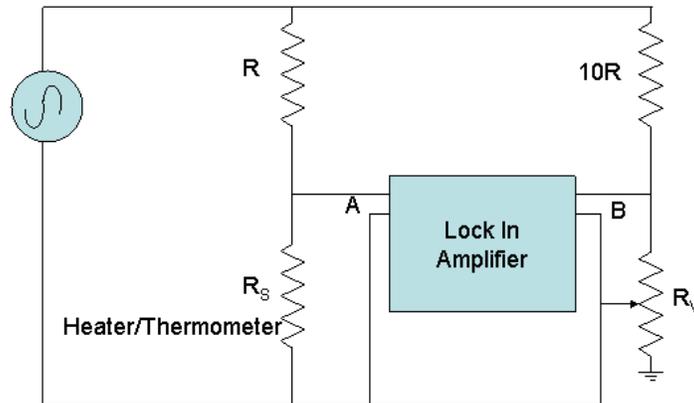


Figure 1: A Block diagram of the measuring circuit for the 3ω technique.

The overall value and phase of the signal across the heater/thermometer (R_S) can be measured on Channel A of the Lock-In. Channel B measures a balanced signal, with a much smaller driving current, effectively creating a bridge circuit where the variable resistor (R_V) balances the voltage drop across R_S at each temperature. This permits observation of the 3^{rd} harmonic without overwhelming the dynamic reserve of the lock-in by measuring Channel (A-B). The current source, either a current calibrator or a signal generator, was swept in both frequency and amplitude, while signals at ω and 3ω were measured on the lock-in amplifier. A control program to automate the procedure, collect the raw data, and signal average was written using LabView.

Several designs for heater/thermometers were investigated and assembled successfully; including films of gold and silver applied by a sputter coater and very fine pure metal wires. The primary interest in developing this technique is for application to a number of metal systems, specifically the actinides, so work focused on test samples that were also metallic. Thus, an important issue in designing the heater/thermometer was to electrically isolate the sample while maintaining intimate thermal conductivity to the sample. Ideally one would sputter thin coats of aluminum metal to the sample surface, and then oxidize these to provide very thin sapphire surfaces to act as electrical insulators. The limits of time and access to an aluminum sputter-coater restricted this avenue, and instead several paints, glues, and epoxies were explored in place of this to provide a thin layer (10-50 microns) of electrical insulation with some success. The experience gained on this front may prove valuable in consideration of future polyimide encapsulated (passivated) samples.

A suitable metal sample was desired that would have a phase transition, and corresponding change in heat capacity, in a readily accessible temperature region. Initially, samples of lead and indium were considered, with the superconducting transition to be studied, which occur at 7.19K and 3.4K, respectively. Over time, it was determined to be easier to work on gadolinium, which has a dramatic change in heat capacity[6,7] at the Curie temperature ($T_C = 293$ K), which is also conveniently close to room temperature, thus saving considerable heating and cooling time.

The Pressure Clamp

We designed a piston-cylinder clamp with several constraints in mind. First, it should be able to obtain a pressure of at least 10 Kbar, while at the same time fitting within the 1" bore of the Quantum Design Physical Property Measurement System, which would provide temperature control and magnetic fields up to 16 Tesla. Consulting with several experts in the high pressure community, we came up with a design which would safely reach our projected goals. In order to manufacture pressure cells, we contacted various machinists both on and off site. We found a machinist who was able to meet the very tight tolerances and the unique materials (both beryllium-copper and Teflon) required for the job and had experience making similar pressure cells for several universities. Fig. 2 shows the final drawings for the pressure cell. As a follow on to this project we would next like to implement this design and carry out a series of unique physical measurements on interesting materials, including plutonium specimens.

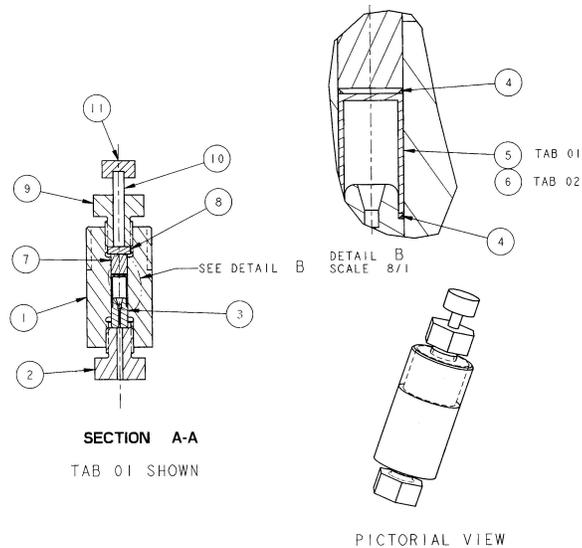


Figure 2: Design of pressure cell used for measuring the specific heat using the 3ω -technique.

Results/Technical Outcome

The third harmonic was readily observable in most of the heaters we constructed, and as one of the initial checks for heater functionality, a sweep of excitation current versus $V(\omega)$ and $V(3\omega)$ was performed. A representative plot is included in Fig. 3, where the magnitude of the 3rd harmonic follows the cube of the excitation current (see equation 4), while as expected from Ohm's Law, the fundamental is linear with current, as shown in the inset. This particular heater was made from half-mil (12.5 μm) platinum wire. With some practice, attaching the wire to a small sample volume while obtaining resistances in the 5-15 Ω range was fairly simple. One challenge was to ensure that very little wire extended beyond the sample, because this complicates the heat flow equation. Attaching the heater/thermometer to a separate wire of an alloy with essentially zero temperature dependence, such as phosphor bronze or rhodium doped platinum, greatly reduced any effects of this nature.

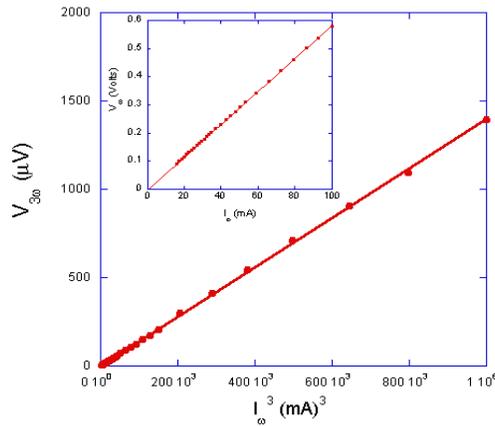


Figure 3: The 3rd harmonic voltage plotted against the cube of the excitation current. Inset shows the linearity of the signal at the fundamental frequency as a function of excitation current.

Similar results were obtained with the gold and silver sputtered films. The temperature dependence was obtained from the following relation [5,8]:

$$\Delta T(\omega) = 2RV_{3\omega}/(\alpha V_{\omega})$$

which is proportional to the slope of Fig. 3. The real (in phase) and imaginary (out of phase) components of $\Delta T(\omega)$ are then plotted as a function of $\ln(\omega)$ as shown in Fig. 4. Some care needed to be taken to compensate for phase shifts arising from the

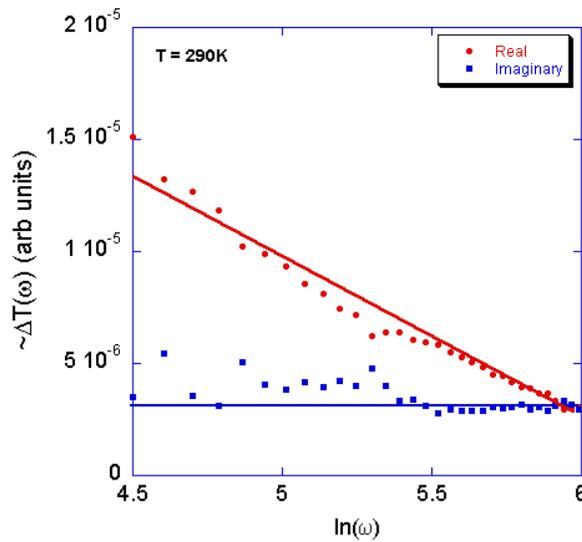


Figure 4: The change in temperature as a function of the natural log of the frequency at 290K. The red line is a fit to the real component data, and the blue is a fit to the imaginary component data.

instruments, and possibly from the electrically insulating barrier. As equation (4) demonstrates, the real component is linear in $\ln(\omega)$, while the imaginary component is independent of ω . The imaginary component is proportional to the thermal conductivity of the sample, while the real component depends on both the heat capacity and thermal conductivity. Exploiting the different functional dependence in ω for the two components enables solution of both the thermal conductivity and heat capacity.

From these data, one can extract a value for the heat capacity of gadolinium in arbitrary units, as shown in Fig. 5 for several points near T_c . The values reported here are relative, and include an additive contribution to the heat capacity due to the insulating layer that has not been removed. It may be possible to treat the insulating barrier separately by measuring a sample at significantly higher frequencies, so that the thermal penetration depth (see equation 5) becomes small compared to the barrier thickness. Due to the smaller heat capacity and typically larger thermal resistance, one may expect that a significantly smaller current could be applied, so that the underlying sample would act as a heat sink. There are indications in the data at the highest frequencies that this may be occurring, but requires further investigation.

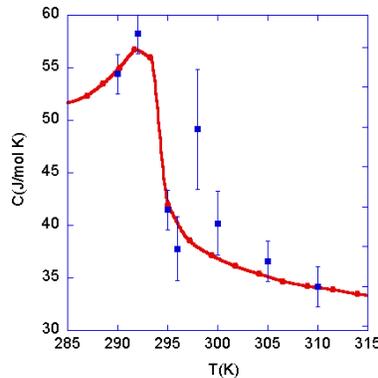


Figure 5: The red curve is the specific heat of gadolinium observed in reference 5. The blue data points show the specific heat values from the 3ω technique in arbitrary units, normalized to the Gd data at 310 K. There is an appreciable contribution from the insulating barrier that limits the ability to provide proper units on these values.

Summary

The development of the 3ω technique for use with pressure cells is shown to be feasible. Implementation is recommended and will provide a unique capability for studying the thermodynamic properties of advanced and special materials. We have shown in this system that even with fairly crude heater/thermometers, one can begin to measure the specific heat of a small sample with this technique. It may be possible to separate the contributions of the different layers by exploring a larger range of frequencies. Alternatively, given access to better fabrication facilities that permit very thin insulating barriers, and the ability to apply much thinner heater/thermometer traces, this technique could be applied more directly to a

number of interesting materials including systems such as plutonium where multi-phase equation of state is an interesting scientific and technical challenge.

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