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Thin film microcalorimeter for heat capacity measurements in high magnetic fields

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Si–N based membrane calorimeters are a promising technology for the study of thermal properties of small quantities of materials in both pulsed and steady-state magnetic fields to 60 T and beyond. We present results that demonstrate our ability to measure the heat capacity of thin film samples from 2–300 K in steady-state fields up to 8 T. These measurements include the magnetoresistance of the Pt and Nb–Si thermometers and focus on confirming that the thermal conductance of the Si–N membrane does not change significantly in magnetic fields. This means the thermal conductance needs to be measured only in zero field, reducing the measurement time in high field. This is particularly important for future measurements in fields up to 60 T. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1461874]

I. INTRODUCTION

Specific heat measurements are an important tool for the investigation of new materials, many of which can be fabricated only in thin film form or as tiny single crystals. The response of these materials to applied magnetic fields is of particular interest for both basic science and industrial applications. Many studies of specific heat in high magnetic fields have been reported for bulk samples, but measurements of thin films have been limited in temperature range or field.[1–4] These techniques are therefore useful only for samples which have a response to magnetic fields at relatively low temperature.

This article describes the application of our existing microcalorimeter technology to the task of measuring heat capacities of microgram samples from 1.5–475 K in magnetic fields up to 8 T and beyond. We briefly review the measurement technique and describe its implementation in magnetic fields before providing example measurements in fields up to 8 T. These measurements include the effect of the magnetic field on the both the high-temperature platinum and low-temperature Nb–Si thermometers and the demonstration of the field independence of the thermal conductance measurement. We present data which establishes an upper limit on the field sensitivity of the calorimeter itself followed by an example of a magnetic sample which shows a field dependent specific heat. We conclude this description of the high field microcalorimeter by predicting possible measurement for thin films and small bulk samples in very high field pulsed and dc fields.

II. PRINCIPLE OF MEASUREMENT

Over the last decade we have reported several measurements of heat capacity of thin films using a membrane based microcalorimeter.[5–11] The design and construction of the microcalorimeter have already been described in detail[12] and require no modification for use in large dc magnetic fields. The calorimeter consists of a silicon frame which supports an amorphous silicon-nitride membrane on which thin-film heaters and thermometers are patterned. The resistive thermometers are patterned from either platinum for measurements above 50 K, or amorphous niobium silicon for use at lower temperatures. The use of these thin-film elements reduces the specific heat of addendas (for a sample area of 2.5 mm$\times$2.5 mm) to $<1\times10^{-9}$ J/K at 2 K and $\approx6\times10^{-6}$ J/K at 300 K.

A small ΔT relaxation method is commonly employed with this microcalorimeter and is convenient for use in dc fields.[13] Large ΔT relaxation and ac methods[14,15] may also be used with this device, and could be better suited for future measurements in pulsed magnetic fields. Determination of the heat capacity using the relaxation method requires measurements of two quantities: the thermal conductance κ of the link between the sample and the bath, and the time constant τ of the sample's relaxation to the temperature of the bath.

Though the techniques used to fabricate these calorimeters result in very small deviations in properties, including C_p and κ, from one device to another, the resistances of the thermometers do vary somewhat. Each measurement therefore includes a calibration of the device's thermometers which requires measurement of the thermometer's resistance at each temperature. This calibration is especially important for the thermal conductance measurement.

To measure this κ, a small amount of heating power P is applied to the sample by causing a known current to flow in the sample heater. A concurrent measurement of the voltage drop across the heater gives the measured heating power P. After thermal equilibrium is reached, the resistance of the sample thermometer is measured. This resistance can be converted to a temperature using the calibration of the thermometer. The thermal conductance is given by $\kappa = P/\Delta T$.

To measure the time constant τ of the relaxation of the sample to the temperature of the bath, we first apply a small current to the sample heater and wait for thermal equilibrium. Then we record the response of the sample thermom-

eter as it cools to the temperature of the bath. For sufficiently small heating power this relaxation follows a single exponential curve. Fitting this measured curve gives the value of the time constant τ. The heat capacity is given by $C = \kappa \tau$.

As applied magnetic fields should have little effect on the thermal properties of the amorphous silicon-nitride membrane and the Pt leads, we expect the thermal conductance of our device to be essentially insensitive to magnetic field. Therefore any field dependence of the heat capacity of a sample will appear as a change in the relaxation time τ. Once this fact is demonstrated, the thermal conductance needs only to be measured in zero field. We do expect the calibration of the Nb–Si thermometers to change slightly at low temperatures due to the small magnetoresistance of this material. However, this magnetoresistance should have little effect on the thermal conductance measurement in high dc magnetic field as long as the sensitivity and reproducibility of the thermometer's response is unchanged. In addition, there should be virtually no effect of the magnetoresistance on the τ measurement, since it does not rely on the calibration of the thermometer.

III. EXPERIMENT

The sample to be measured is deposited on a thermal conduction layer at the center of the membrane. This layer is normally ≈ 2000 Å of either gold, copper, silver, or aluminum which ensures the sample is in thermal equilibrium with the heater and thermometers. Thin film samples are typically evaporated or sputtered directly on the membrane through a shadow mask. We have also measured single crystals with masses of ≈ 200 μg and powdered samples with this membrane calorimeter.[9,10]

Once the sample is deposited or attached to the membrane, wires are bonded to the calorimeter's heaters and thermometers and the calorimeter is mounted onto a copper stage in a cryostat. The area around the calorimeter is pumped to high vacuum ($< 1 \times 10^{-7}$ Torr) and this vacuum is maintained throughout the measurement. The vacuum around the calorimeter is important because small amounts of gas or ice on or around the membrane unpredictably and irreproducibly alter the measured thermal conductance and tau. Once the cryostat is evacuated, we cool in either liquid helium or liquid nitrogen. A small liquid helium pot in direct thermal contact with the sample stage allows the sample to be cooled to 2 K while still maintaining high vacuum in the space around the calorimeter. For measurements in high fields, the cryostat is inserted in an 8 T superconducting magnet.

The temperature of the copper block is monitored with a Lake Shore Cernox temperature sensor and temperature controller. The Cernox sensor was chosen for its low field sensitivity. Magnetic field induced error ($\Delta T/T$) is less than 1% at all temperatures in up to 8 T.[16] All measurements of the device thermometers are made with an EG&G lock-in amplifier and an ac resistance bridge which we previously described.[12] The sequence of measurements is performed and recorded through general purpose instrument bus (GPIB) connections by a PC running Labview.
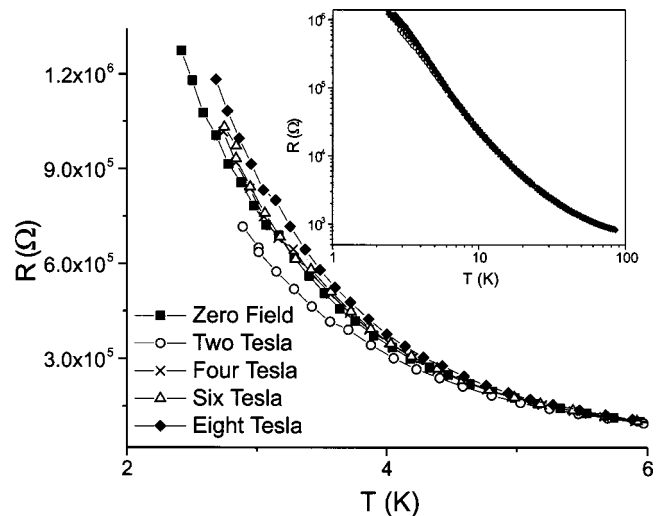

FIG. 1. The resistance of the Nb–Si thermometer at low temperatures in fields up to 8 T. Below 6 K, a magnetoresistance is apparent. This magnetoresistance is initially positive, but becomes negative with increasing field. The inset shows a broader range of temperatures on a log-log plot.

IV. RESULTS

In order to demonstrate the calorimeter in high magnetic fields we performed experiments on several samples in various temperature ranges. A demonstration of our device as a high field calorimeter requires verification that the measurement of thermal conductance is insensitive to field, as well as demonstration that field induced changes in τ result from field-dependent heat capacities.

Figure 1 shows the resistance versus temperature from 2–6 K for a Nb–Si thermometer in zero field as well as 2, 4, 6, and 8 T applied magnetic fields. The shifts in the resistance curve at these temperatures indicate the small magnetoresistance of the thermometer. The thermometer's resistance is reduced by a 2 T magnetic field, indicating an initially negative magnetoresistance. Higher magnetic fields increase the resistance, though the magnetoresistance remains fairly small. The inset in Fig. 1 is a log–log plot showing 2–80 K which is the full temperature range for this low temperature thermometer. The field-induced change in the resistance above 12 K is less than 1%. Even at low temperatures the *slope* of these curves is not significantly changed by the applied field. This indicates that the sensitivity of the thermometer is sufficiently independent of field to be used to determine κ. We have also verified that the platinum thermometers show no influence of applied fields in their useful temperature range.

Figure 2 is a plot of the magnetoresistance $\Delta R/R$ of the Nb–Si thermometer versus applied field. The pattern of negative low-field and positive higher-field magnetoresistance is clear and remains up to 12 K. The magnitude of the magnetoresistance decreases with increasing temperature, with the maximum value determined for this data of $\approx 15\%$. Also note that while these magnetoresistances are reasonably small, they are larger than the 1% values expected from the Cernox temperature sensor.

The field dependence of the calorimeter's thermal conductance κ is shown in Fig. 3. There is virtually no effect of
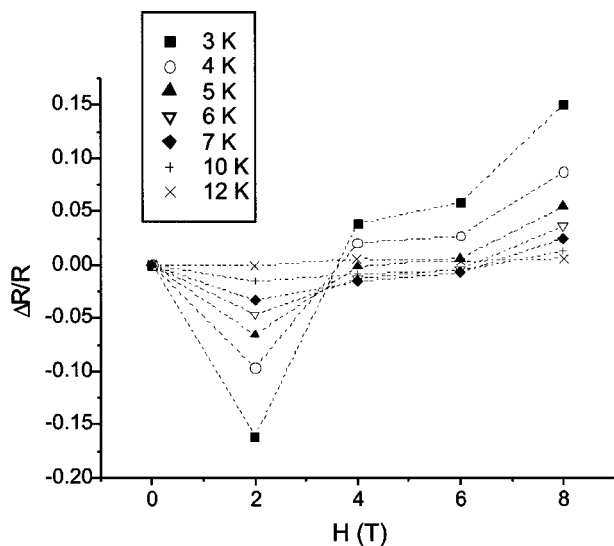
FIG. 2. The magnetoresistance $\Delta R/R$ of the same Nb–Si thermometer in fields up to 8 T. The magnetoresistance is largest at low temperatures and vanishes by 12 K.

FIG. 4. The specific heat of addenda in 0 and 8 T. The conduction layer is 2000 Å of Au with an underlayer of Ti. The inset shows the time constant τ. Neither τ nor the specific heat change with field.

applied magnetic field on κ. This verifies that the Nb–Si thermometers still give reliable measurement of temperature in dc fields up to 8 T.

The heat capacity of the calorimeter from 50–350 K is shown in Fig. 4. This heat capacity is the addenda, which must be subtracted from the total specific heat measured after a sample is deposited on the calorimeter. This addenda includes contributions from the Si–N membrane, the Pt leads, heater, and high temperature thermometers, the Nb–Si low-temperature thermometers, and a ≈ 2000 Å gold layer with a thin titanium underlayer. As expected the total specific heat is independent of applied field.

Figure 5 shows $\tau = C_p/\kappa$ as a function of field at several temperatures between 4–10 K for a calorimeter with a FeCr multilayer sample. Though one might have expected some field dependence of C_p for this sample, this was not found. Instead the measurement sets a limit on the sensitivity of the calorimeter to applied field. The resulting upper limit on the

field dependence of τ at low temperatures is ≈ 2 ms. This indicates that the specific heat varies by less than 4×10^{-10} J/K. The implications of this data and other measurements on this material are reported elsewhere.[11]

The low temperature τ and C_p for an $a\text{-}Gd_xSi_{1-x}$ sample plus addenda appears in Fig. 6. Data and analysis for this amorphous magnetic semiconductor will be discussed in full detail elsewhere.[17] Figure 6(a) is a plot of the relaxation time τ for this device at low temperatures. The inset shows the same data up to 80 K. The large values of τ seen here are caused by a-Gd–Si's large low temperature specific heat. Values of τ for materials with more typical low temperature specific heat are nearly two orders of magnitude smaller and do not show a pronounced upturn at lower temperatures. The magnetic field induced shifts appear small relative to the zero field values, but are much larger than the upper limit on the device's field sensitivity established by the data in Fig. 5. Figure 6(b) shows this device's heat capacity, C_{total}, as well as the contribution of the addenda. The shifts in τ and therefore in C_p are characteristic of this spin glass sample and change with changing Gd concentration.
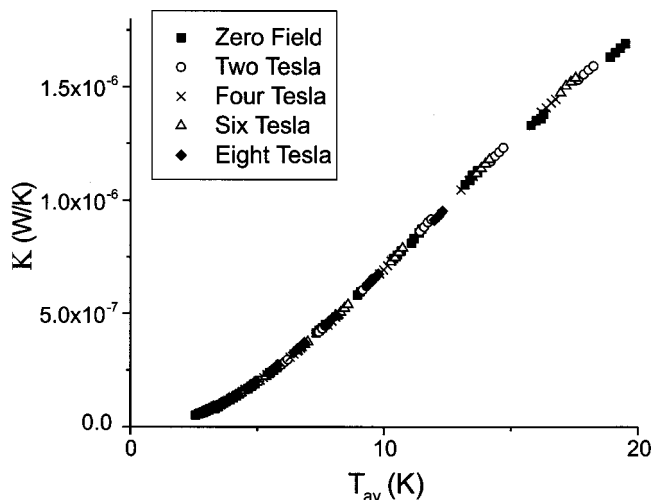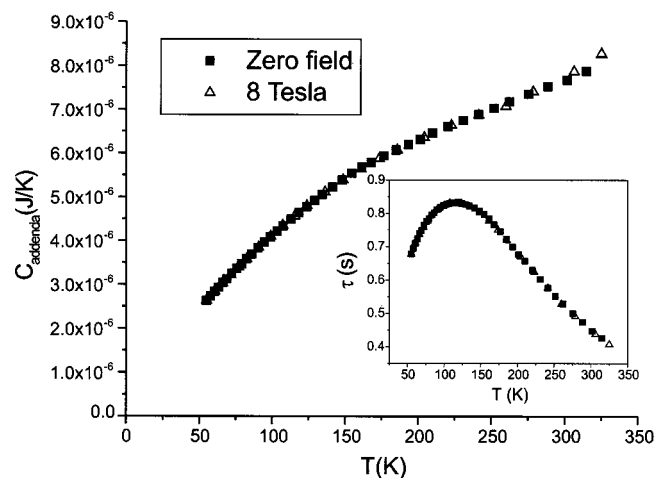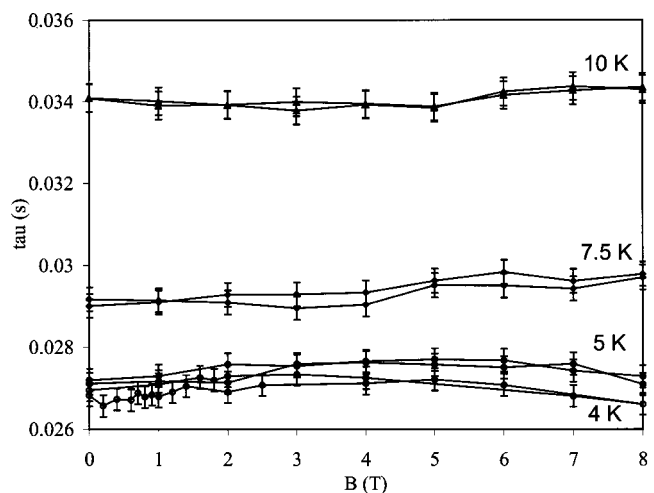

FIG. 3. The thermal conductance κ of the calorimeter in fields up to 8 T. There is little effect of the magnetoresistance shown in Fig. 1.

FIG. 5. The dependence of tau on magnetic field at several temperatures between 4–10 K. The magnetic field dependence is very small.
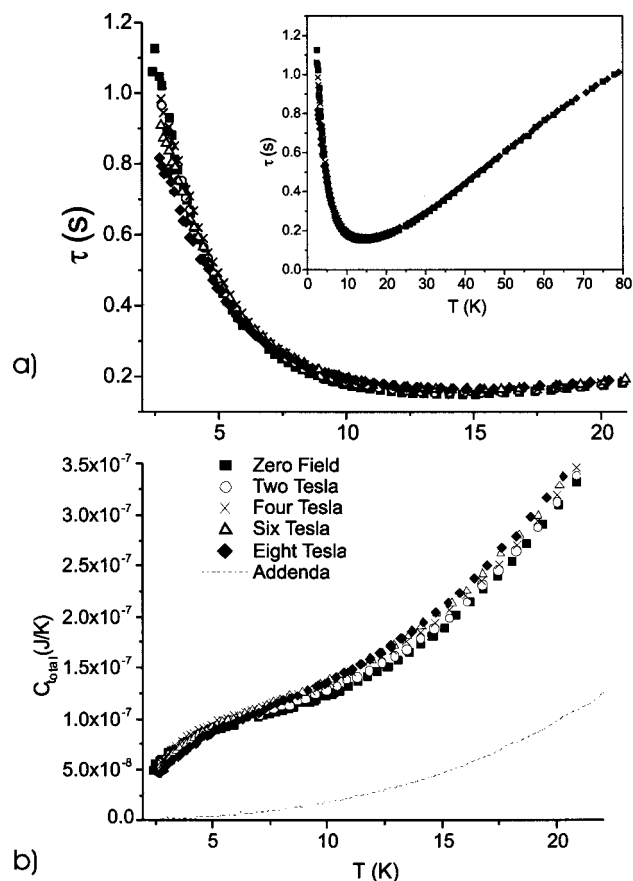
FIG. 6. (a) Time constant τ as a function of temperature in magnetic fields up to 8 T for a device with a $\approx$4000-Å-thick film sample of a-$Gd_{0.07}Si_{0.93}$. The small shifts in τ are the signature of the field dependent specific heat of this spin glass. The inset shows the same measurement from 2–80 K. The large upturn in τ below 15 K is due to the large low temperature specific heat of a-Gd_xSi_{1-x}. (b) The resulting heat capacity of this device. The dotted line indicates the field independent contribution of the addenda, which is $\approx$1% of the total specific heat at low T.

V. OUTLOOK-HIGH FIELD MEASUREMENTS

We have demonstrated that our membrane microcalorimeter is an effective tool for measuring specific heat of thin-film and other small samples from 2–300 K in applied dc magnetic fields up to 8 T. These results, particularly the re-producibility of the thermal conductance in various magnetic fields, lead to the consideration of our microcalorimeter technology as a solution for the measurement of specific heats of any small samples in fields up to 30 T and beyond. In these types of measurements, the ability to rely on thermal conductance values measured in zero field means only τ need be measured in high field. Because the magnetoresistance of the thermometers has no effect on the tau measurement, the thermometers need not be calibrated in field. These facts save valuable high field data acquisition time. There are yet many challenges to adapting these microcalorimeters for use in very high field systems, including the demands of space in small magnet bores, assuring thermal stability of the calorimeter, and measuring the impact of the thermometer's magnetoresistance on pulsed field measurements.

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