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AN APPARATUS TO DETERMINE THE HEAT CAPACITY AND THERMAL CONDUCTIVITY OF A MATERIAL FROM 1 TO 300 K IN MAGNETIC FIELDS UP TO 9 T*

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INTRODUCTION

Magnetic refrigeration is a new technology that potentially offers refrigeration efficiencies > 50% of Carnot, compactness, and high reliability. Studies[1] indicate that ∿ 35% of Carnot efficiency is generally the best that is now possible for gas compression/expansion systems and, at that, only for very large plants; for smaller machines, the fraction of Carnot efficiency can become very small, e.g., 1-W refrigerators generally operate at 2-3% of Carnot efficiency. For magnetic refrigerators, the compression/expansion processes are replaced by a cycle involving the application/removal of a magnetic field to either a paramagnetic or ferromagnetic material (generally, paramagnets are used below ∿ 20 K and ferromagnets above). The thermodynamic cycles in gas and magnetic systems are analogous.

Central to the development of magnetic refrigerators is the characterization of magnetic working substances. Among the key properties for which we require data are the heat capacity (from which we derive the entropy) and the thermal conductivity as functions of temperature and magnetic field. Accordingly, at the Los Alamos National Laboratory, we have designed and constructed an apparatus to make measurements of these quantities over the range 1 to 300 K at fields up to 9 T. In this paper we describe the methodology of these measurements, the versatile apparatus for making them, and results on GdNi,[2] the first sample measured.

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METHODOLOGY OF HEAT CAPACITY/THERMAL CONDUCTIVITY MEASUREMENTS

Several methods for measuring heat capacity can be used at low temperatures.[3] Typically, these involve either a steady state, adiabatic), transient, relaxation, or differential technique.[5-11] Although each of these techniques has advantages and disadvantages, -- some are limited by such factors as sample size or temperature range -- our apparatus is not limited to a specific technique.

The zero-field entropy of magnetic materials can be obtained by integrating the zero field heat capacity as a function of temperature. The change in entropy with applied field can be obtained by integrating the heat capacity measured in various applied fields or by measuring the adiabatic temperature changes as a function of temperature and field. Our apparatus was designed to take advantage of either of these methods as well as to allow the heat capacity to be measured using several different techniques. For example, from 1 to 20 K (where heat capacities are small and addenda problems are more severe), a relaxation technique can be used, and either a steady state or a transient technique can be used from 20 to 300 K. The thermal conductivity of magnetic materials can advantageously be obtained concurrently using a transient heat flow technique; this generally yields the thermal diffusivity, but by measuring both the short- and long-time behavior (illustrated in Fig. 1) it is possible to obtain both the heat capacity and the thermal conductivity. From a measurement of the time $t_{1/2}$ (Δt in Fig. 1), taken to reach half the maximum temperature rise after a heat pulse, the diffusivity D can be calculated. Measurements of the energy contained in the heat pulse and the equilibrium temperature change (ΔT in Fig. 1) allow determination of the heat capacity C of the sample. Because $D = \kappa/\rho C$, the thermal conductivity κ can then be obtained if we know the density ρ. Of the several transient methods available,[12] we selected one that uses a long rod having a heater on one end and a very small support on the other end. The

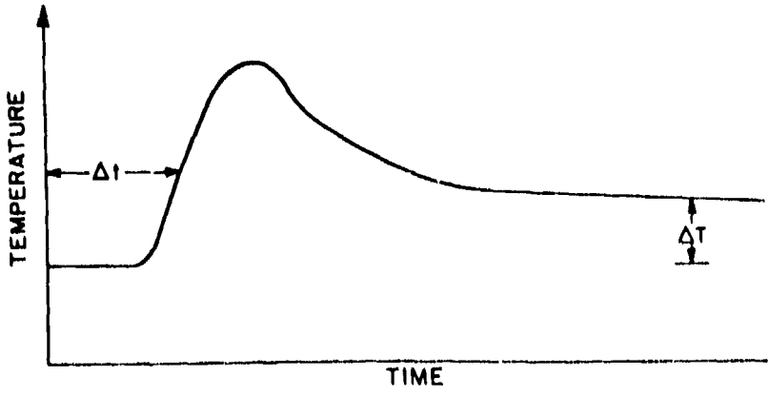

Fig. 1. A typical temperature vs time plot in a transient thermal diffusivity measurement.

temperature profile after a heat pulse can be obtained by solving the diffusive heat flow equation

$$D\frac{\partial^2 T}{\partial x^2} - \frac{\partial T}{\partial t} = 0 \quad . \tag{1}$$

The solution with the boundary conditions for a short heat pulse causing an initial ΔT_o over length ΔX_o is given for length L by

$$T(L,t) = (\Delta T_o/L)[1 + 2\sum_{n=1}^{\infty}(-1)^n \exp(-n^2\pi^2 Dt/L^2)]\,\Delta X_o \quad . \tag{2}$$

The diffusivity can be obtained from Eq. (2) in terms of the measured value of $t_{1/2}$ according to

$$D = 1.370\, L^2/(\pi^2 t_{1/2}) \quad . \tag{3}$$

One of the difficulties in using this transient technique is that the response time of the temperature sensor (thermocouple) must be short. The response time of the thermocouple is a function of its size and the method of attachment to the sample; if the size of the thermocouple is sufficiently small, the method of attachment will determine the response time. We have used thermocouples with a tip of $\sim$ 13 μm diam. attached to a sample with varnish, but the response time was still an order of magnitude too slow. Consequently, we are investigating the possibility of vapor depositing an electrical insulating layer and a thermocouple onto a sample to obtain a satisfactory response time.

When the steady state method is used, a measured quantity of heat is added to the sample and its equilibrium temperature change allows the heat capacity to be determined from $Q = m\,C\,\Delta T$, where Q is the heat added and m is the mass of the sample. The sample is then stabilized at a new temperature and the procedure repeated. Obviously, the heat capacity of the addenda, and heat losses from conduction and radiation, must be considered. This is the method that we have used to date, primarily because of the inadequate thermocouple response time mentioned above. However, this method has not been without its difficulties -- primarily that of obtaining an adiabatic, isothermal environment, and determining the effect of the addenda on the measurements.

TEST APPARATUS

The system that we designed and built to measure heat capacity and thermal conductivity is shown in Fig. 2. The instrumentation for the test apparatus is shown schematically in Fig. 3. The dewar has an overall height and diameter of 2.16 m and 0.33 m, respectively. Three stages of isolation between the sample and the

liquid helium bath allow the sample temperature to be varied from ~ 1 K to > 300 K by independently heating the sample, can 1, and can 2. Stainless steel supports separate the cans from each other, and a thin fiberglass sample holder isolates the sample from can 1. The heaters on the sample, can 1, and can 2 are made from Evanohm wire to avoid any temperature dependence of resistance. The heaters on cans 1 and 2 are distributed such that both the top and bottoms of the cans are heated. Copper strips from the top to the bottom of the stainless steel cans provide a uniform temperature for the cans. The cans are made of stainless steel to avoid eddy current heating when they are moved rapidly in the magnetic field. The electrical leads for the heaters and the temperature sensors are routed through the center tube. They are attached to a heat sink at the top of can 3 to prevent heat conduction from room temperature to cans 1 and 2. Furthermore, the electrical leads entering can 1 are attached to a heat sink anchored to the top of can 1 to prevent heat conduction to the sample (the sample and can 1 are maintained at near the same temperature to provide an isothermal, adiabatic environment to reduce or eliminate conduction and radiation losses during the measurement).

The pulse generator requires a 50-Ω load for maximum power output and has a 200-W peak power output with a pulse width variable from 1 μs to 10 ms. The sample and can temperatures are measured with both carbon-glass resistors and gold (with 0.07 at.% iron)/chromel-P thermocouples. These thermocouples have a temperature sensitivity of about 10 μV/K at 2 K and about 22 μV/K at 300 K.[12] Carbon-glass resistors are used for the

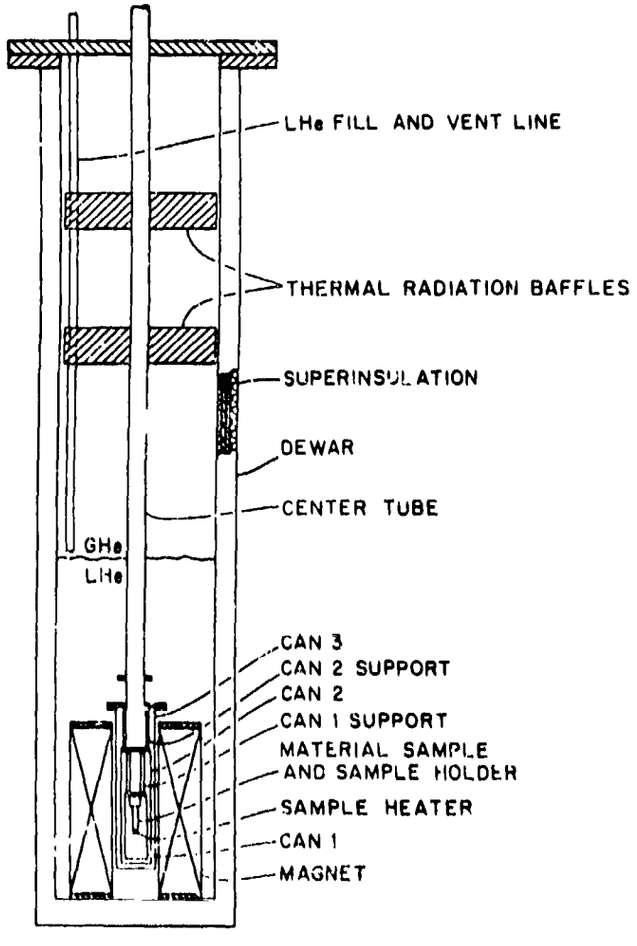

Fig. 2. Diagram of heat capacity/thermal conductivity apparatus. Not to scale.

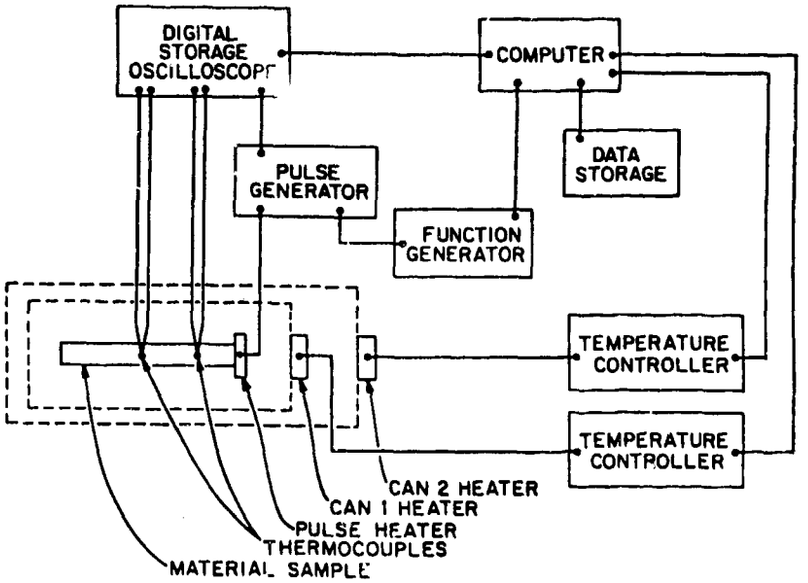

Fig. 3. Instrumentation system for the heat capacity/thermal conductivity measurements.

temperature controllers because they are relatively insensitive to the magnetic field and have a larger temperature sensitivity than gold/chromel thermocouples. The superconducting magnet, made from NbTi wire, is capable of producing a maximum field of 9 T.

TEST PROCEDURE/TECHNIQUE

The sample temperature is set by using the sample heater and the can 1 heater; the temperature of can 1 is maintained by a temperature controller. Can 2 provides an isothermal environment around can 1 and is also fitted with a temperature controller. When the desired temperatures and magnetic field are established, a signal through the function and pulse generators delivers an electrical pulse of the desired voltage and duration to the sample heater. At the same time, the digital storage oscilloscope is triggered to record the heater pulse. The pertinent data -- sample temperature, pulse duration and voltage, and can 1 and 2 temperatures -- are received by a microcomputer, stored on a floppy disc, and displayed for evaluation. If satisfactory, the next temperature and/or magnetic field condition is established and this procedure repeated.

The adiabatic magnetization/demagnetization temperature change is obtained in a manner somewhat similar to that above. However, instead of applying a heat pulse, the sample is raised out of the magnetic field to give the demagnetization temperature change and then lowered back into the bore of the magnet to get the temperature change upon magnetization. The sample is moved into and out of the

magnet bore by using an air-driven piston mounted above, and attached to, the center tube (which is attached to can 3 and extends through the top flange).

TYPICAL RESULTS

Measurements were made on a sample of GdNi, 24.5 mm long and 6.4 mm diam., using the steady state heat capacity method (thermal conductivity was not measured). The zero-field heat capacity data are shown in Fig. 4 with a polynomial least squares fit to the data. For these measurements, a thermocouple and a carbon-glass resistor were mounted on the sample along with a noninductively wound Evanohm heater. The sample was held in position by a slotted fiber-glass tube that was attached to the top of can 1. The heat capacity, determined from the equilibrium temperature change obtained by adding a heat pulse to the sample, was adjusted by consideration of: (1) the short term (almost instantaneous) radiation loss as a result of the difference between the maximum heater temperature and the can 1 temperature; (2) the heat loss by conduction through the sample support from the sample to can 1; (3) the heat loss by conduction through the wiring (heater, carbon-glass resistor, and thermocouple) from the sample to the heat sink in can 1; and (4) the heat capacity of the addenda (carbon-glass resistor, thermocouple, sample holder, and heater).

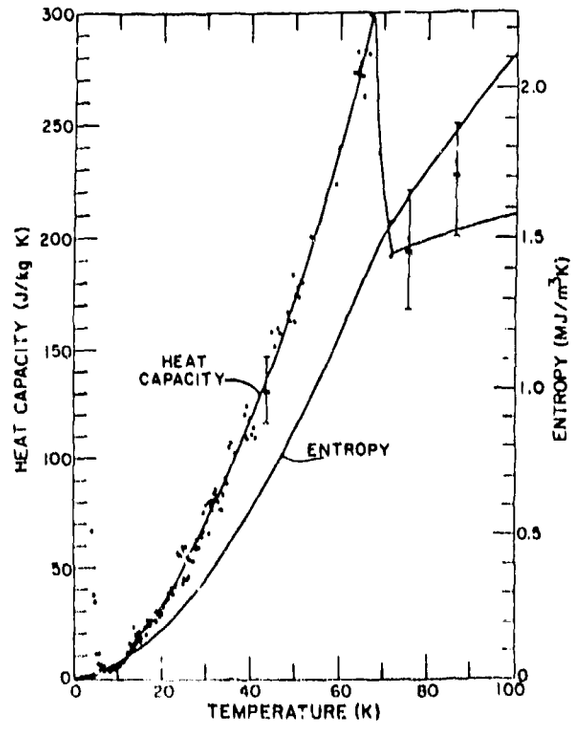

Fig. 4. Heat capacity and entropy of GdNi.

The data contain both systematic and statistical errors. The systematic errors consist of those in temperature-sensor calibration, in the measurements (the data acquisition unit had a resolution of ~1 μV), and errors as a result of a nonadiabatic, nonisothermal environment and magnetic field effects on the temperature sensors. The statistical errors, from such factors as the uncertainty in the corrections applied in consideration of the addenda, should be minimized by the use of a least squares fit to the data. In considering the many factors involved in this, the first measurement made using the apparatus, we estimate that the data shown has a precision of about 8 to 10% and an accuracy of a few percent.

The heat capacity, as expected, exhibits a large magnetic anomoly with a maximum at ∿ 67 K (the Curie temperature). The background under the magnetic contribution shows the large temperature dependence of the lattice contribution to the heat capacity in the temperature range covered. The sample entropy shown in Fig. 4 was obtained by a numerical integration of

$$S(T_f) = S(T_i) + \int_{T_i}^{T_f} \frac{C(T)}{T}\, dT \quad , \tag{4}$$

where the subscripts f and i refer to final and initial values of T. Results for the adiabatic-magnetization/demagnetization-temperature-change upon moving the sample in and out of the magnet are shown in Fig. 5. Near the Curie temperature and with a field change of 5 T, a temperature change of ∿ 6 K was obtained. Note that the maximum temperature change occurs at different temperatures for magnetization and demagnetization.

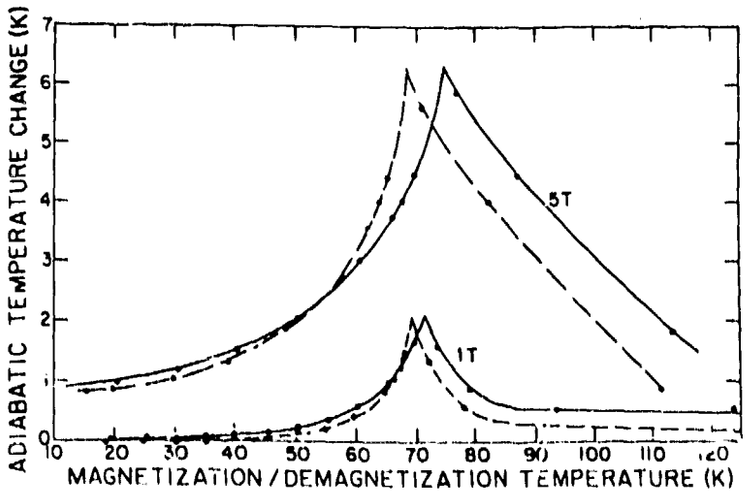

Fig. 5. Adiabatic-magnetization/demagnetization-temperature change for GdNi.

SUMMARY

We have a rather general experimental apparatus for measuring heat capacity and thermal conductivity over a wide temperature range and as a function of magnetic field. The apparatus has also been used to calibrate temperature sensors (carbon-glass resistors, germanium resistors, and gold-iron/chromel-P thermocouples) as a function of temperature and magnetic field. The apparatus could be used to make resistivity measurements also, although this has not yet been done. The apparatus is being improved to overcome the difficulties encountered and to improve the precision and accuracy of the measurements.

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