Magnetocaloric cooling observed in polycrystalline $YBa_2Cu_3O_x$

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We report the observation of magnetocaloric cooling in polycrystalline $YBa_2Cu_3O_x$ at $T \ll T_c$. By using a temperature measurement, the field-induced heating or cooling in an adiabatic environment has been measured for magnetic fields up to 300 Oe applied at constant ramp rates in the absence of a transport current. In hysteretic runs at 6.5 and 7.1 K cooling of the order ~0.35 mK has been observed at applied fields up to 230 and 150 Oe, respectively. For fields larger than these heating occurs and takes over as the dominant effect. The cooling is proportional to the square of the applied field and independent of the ramp rate of the magnetic field. The volume average magnetic-flux density B has been simultaneously measured and found to increase as the square of the applied field up to 150 Oe and then to increase nearly linearly with applied field up to 300 Oe. Using classical thermodynamic arguments, we find that 0.001–0.0045 % of the material has returned to the normal state in an applied field of 100 Oe at 7.1 K.

I. INTRODUCTION

When an external magnetic field greater than H_c/H_{c1} is applied to a type-I or type-II superconductor (with a small demagnetizing coefficient) in an adiabatic environment, both irreversible heating and reversible cooling can simultaneously occur. The irreversible heating is caused by the induced eddy currents flowing in the "quasinormal" regions which try to oppose the entering magnetic field. For a type-II superconductor if, in addition, the magnetic field is varying with time after the introduction of the normal state material, further heating may occur because of the changing magnetic structure in the material. The reversible cooling in both types of superconductors occurs because of the destruction of the superconducting state in a small portion of the sample, which raises the free energy of the material. This will result in a decrease in the sample's temperature. The decrease in the sample's temperature will depend on the magnitude of the entropy change as the material passes from the fully superconducting state to the normal state. For a type-II superconductor with $H_{c1} < H \ll H_{c2}$ the magnitude of the cooling will occur continuously with H and thus will be harder to detect than in a type-I superconductor. Further, at these low fields only a small fraction of normal state material will be created, implying a much smaller change in entropy.

Observation of a magnetocaloric cooling effect in a type-I superconductor was made in 1934 by Mendelssohn and Moore[1] and later by Keesom and Kok.[2] Observation of magnetocaloric cooling in a type-II superconductor was made in 1964 by Hake and Barnes[3] and later by Ohtsuka.[4,5] The observation of a magnetocaloric cooling effect in the high-temperature superconductor $YBa_2Cu_3O_x$ has been previously reported by Leyarovski *et al.*[6] for $T > 45$ K. We report the observation magnetocaloric cooling in the high-temperature superconductor $YBa_2Cu_3O_x$ at 6.5 and 7.1 K for applied magnetic fields up to 230 and 150 Oe with ramp rates $dH/dt = 268$ and 178 Oe/s. In this experiment, we have simultaneously measured the temperature change (ΔT) and the magnetic-flux density (B) as a function of the applied field (H).

By equating the entropy of the superconducting to normal state transition we have calculated, using reversible thermodynamics,[7] the maximum allowed cooling for an $YBa_2Cu_3O_x$ sample assuming it changes adiabatically from its fully superconducting state to its fully normal state. The results show that if the sample's initial temperature were 7.1 K (used in our experiment) then the final temperature after cooling would be $\sim 2.5 \pm 1$ K.[8]

II. EXPERIMENT

A high-T_c superconductor consisting of $YBa_2Cu_3O_x$ was made by standard ceramic techniques. Sample preparation and characterization have been described elsewhere.[9] The sample used in our experiment was cut from a disk 5.08 cm in diameter and 0.36 cm thick. The sample's density was measured to be 5.43 g/cm^3. The final dimensions of the rectangular sample were $4.578 \times 2.35 \times 0.36$ cm^3. A large length to thickness ratio in the direction of the applied magnetic field was chosen to reduce the demagnetizing effects which have been ignored in our analysis.

ac inductance measurements showed that a superconducting transition occurred with an onset of 93 K and a transition width of about 1.5 K. Low voltage electrical resistivity measurements were made by standard four-lead techniques. Results show a normal state resistivity of 1.1 mΩ cm at 300 K and confirmed the sample's T_c. Using an electric field criteria of 1 μV/cm, transport critical current measurements taken at 4.85 K show that the sample's J_c was 290 A/cm^2 for a sample whose transverse dimensions were 0.34×0.045 cm. X-ray data have shown that the sample is single phase to within 5%.

The experimental setup used to measure the magnetization and the change in the sample's temperature (ΔT) is shown in Fig. 1. The vacuum chamber was cooled via helium exchange gas to an ambient temperature ranging from 4.85 to 7.1 K and then evacuated to increase the thermal isolation of the sample.

The accuracy of the thermal measurement and calibration of the pickup coil, as well as the magnetic field, were verified by placing a sheet of lead with the same dimensions (and therefore small demagnetizing factor) as the $YBa_2Cu_3O_x$ sample in the pickup coil and subjecting it to a time varying magnetic field. The temperature measurement of the lead sample showed magnetocaloric cooling (~ 0.11 K) at 5.0 K for fields slightly greater than H_c. No heating >50 μK was observed in the Pb sample below H_c. Above H_c and after (~ 0.2 s) the initial cooling, the Pb sheet showed heating ~ 0.24 K for $H = 655$ Oe and $dH/dt = 219$ Oe/s. The simultaneous magnetization measurement allowed us to calibrate the pickup coil and the magnetic field. Further details about the data collection in this experiment (thermometry calibration and sensitivity, pickup coil calibration, etc.) have been discussed in more detail elsewhere.[10]

A series of triangular magnetic-field sweeps were performed on the sample at ambient temperatures of 6.5 and 7.1 K. In these series both the magnitude and the pulse duration were varied to study the rate dependence of the cooling effect as a function of the applied field. The maximum (minimum) field used in this experiment was 300 Oe (100 Oe) and the longest (shortest) ramp duration was 2.5 s (0.5 s). Magnetic-field ramps longer than these became increasingly difficult to analyze because of heat loss to the environment due to lack of good thermal isolation. Each series consisted of 4 sweeps (1 magnetization, 3 hysteretic),[11] for a particular field range and duration. After each series the sample's temperature was raised above T_c so that any trapped flux in the material would be expelled and the sample would be returned to its magnetization state before the next series of field sweeps began.

The specific heat $C(T)$ between 4.85 and 7.5 K was then measured, *in situ*, by applying a triangular current pulse (0.5 s duration) to the carbon resistor and measuring the change in temperature of the sample with a Lakeshore Cryotronics DT-470 silicon diode as a function of time. The specific heat values obtained in this way are larger by $\sim 25\%$ than those reported by Fisher *et al.*[12] but smaller ($\sim 10\%$) than some reported by Muller *et al.*[13] Although our sample was not held under very good adiabatic conditions, the measurement of the magnetocaloric cooling and specific heat under comparable conditions will reduce the error resulting from the lack of a good adiabatic environment.

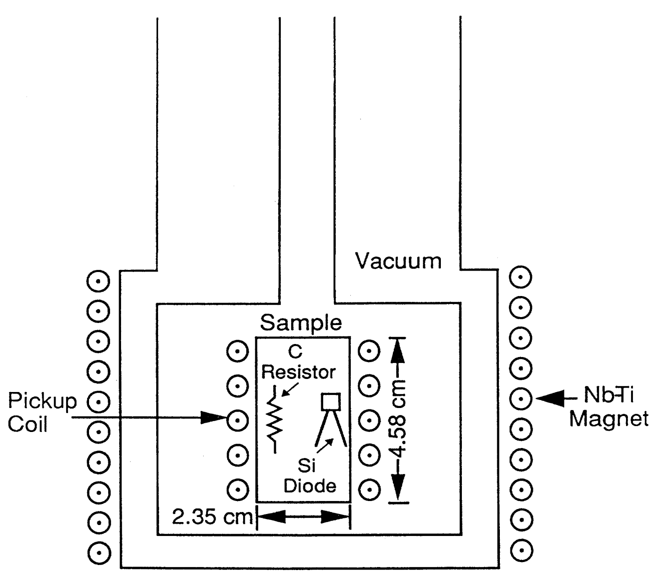

FIG. 1. Schematic drawing of experimental apparatus showing both the thermal and magnetization measurements. The carbon resistor and silicon diode are in intimate thermal contact with the $YBa_2Cu_3O_x$ sample.

III. RESULTS

A. Magnetocaloric heating

Figure 2 shows heating for increasing H in a magnetization run at 7.1 K with $dH/dt = 178$ Oe/s. Results show that only heating of the sample was observed for magnetization runs even when the ambient temperature was between 6.5 and 7.1 K (where cooling was observed in the subsequent hysteretic runs). For the magnetization run, the temperature increase in the sample was fitted with a linear regression of the form $\Delta T = A + CH$, where $A = (-5.8 \pm 0.2) \times 10^{-4}$ K and $C = (7.8 \pm 0.2) \times 10^{-6}$ K/Oe for $H > 80$ Oe.

Only heating was observed when the ambient temperature was below 6.5 K independent of the applied field for both magnetization and hysteretic runs. The heating behavior observed below 6.5 K has been described in more detail elsewhere.[10]

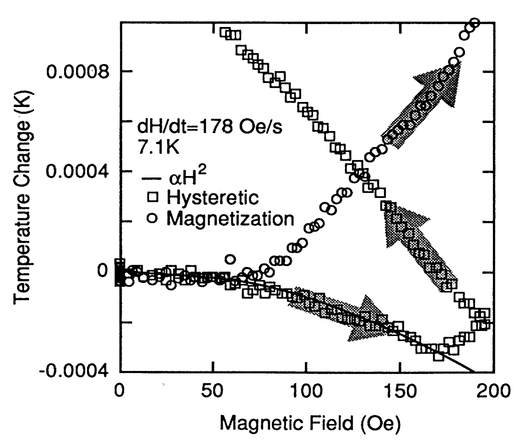

FIG. 2. Plot of ΔT vs H for both magnetization (○) and hysteretic (□) runs. The solid line is $\propto H^2$. Arrows indicate increasing and decreasing H. The data for decreasing H in the magnetization run have not been included because they exceed the scale of the figure.

There was no appearance of the cooling effect above 7.5 K. The lack of observation of magnetocaloric cooling above 7.5 K is most likely the result of experimental complications resulting from a slower thermal response time of the carbon resistor as the ambient temperature increased. Therefore, we cannot report a maximum temperature for which magnetocaloric cooling is observable in this material. Leyarovski *et al.* have reported magnetocaloric cooling from 45 to 90 K; however, below 30 K the cooling effect became smaller than the sensitivity of their measurement (~ 1 mK).

B. Magnetocaloric cooling

Figure 2 also shows a parabolic reduction in the sample's temperature for an increasing applied field up to ~ 150 Oe at 7.1 K in a hysteretic run with $dH/dt = 178$ Oe/s. As one can see from the shape of this curve, cooling proportional to H^2 was observed up to ~ 150 Oe. Above ~ 150 Oe, heating begins to occur and continues to rise out to the maximum field (~ 195 Oe). Further heating was observed as the magnetic field began decreasing, demonstrating the irreversibility of the field-induced heating effect. Magnetocaloric cooling was only observed when the sample's initial temperature was between 6.5 and 7.1 K and for hysteretic field sweeps (see Fig. 2).

The decrease in the sample's temperature with increasing field had an approximate form $\Delta T = (-1.12 \pm 0.1) \times 10^{-8}$ $[H(\mathrm{Oe})]^2$ K (see Fig. 2). Leyarovski *et al.* report a nearly linear decrease in temperature for increasing applied field up to 120 Oe for $T = 45.77$, 81.64, 86.41, and 90.24 K. Deviations from linear behavior in their data were explained as heating effects. No cooling effects $\propto H^2$ were reported in their data.

The decrease in temperature was found to be independent of dH/dt for the field ramps used in this experiment which ranged from 40 to 600 Oe/s. The magnitude of cooling for the three consecutive hysteretic runs was reproducible to within 5% for each series of magnetic field sweeps.

C. Magnetic-flux-density measurements in magnetization and hysteretic field sweeps

Figure 3 shows the *B*-*H* relation for both magnetization and hysteretic runs at 7.1 K with $dH/dt = 178$ Oe/s. At 7.1 K in hysteretic runs, the simultaneous magnetic-flux-density measurements show that for increasing H, B increases as the square of the applied field from 30 to 150 Oe. For fields larger than 150 Oe, B tends towards a linear dependence on H. Below 30 Oe the magnetic-flux-density data were too inaccurate to determine its field dependence. For the 30–150-Oe field region where only cooling was observed, the approximate functional form of B (in Gauss) is $B = (6 \pm 2) \times 10^{-4}$ $[H(\mathrm{Oe})]^{\alpha}$ G, where $\alpha = 2.1 \pm 0.1$ for a hysteretic run with $dH/dt = 178$ Oe/s. For the same field ramp but at fields > 150 Oe, B tends towards a linear dependence on H where the approximate functional form is $B = (0.15 \pm 0.05)$ $[H(\mathrm{Oe})]^{\beta}$ G, with $\beta = 1.15 \pm 0.05$ (see Fig. 3). In magnetization runs, the

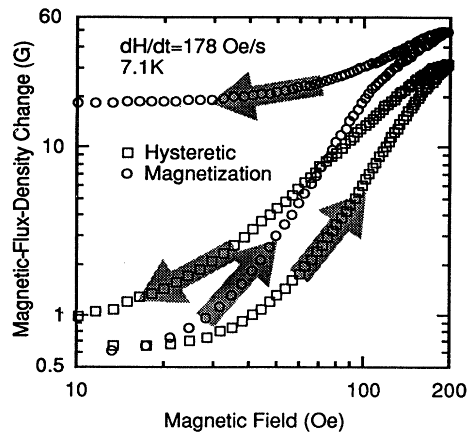

FIG. 3. Log-log plot of $B - B_r$ vs H for both magnetization ($\bigcirc$) and hysteretic ($\square$) field sweeps where B_r is the remanent flux density. Arrows indicate increasing and decreasing H.

tendency towards a near linear *B*-*H* region starts at lower fields ~ 100 Oe.

Data taken at 4.85 K show that B is rate dependent up to ~ 100 Oe(~ 150 Oe) in magnetization (hysteretic) runs. Further, for fields between 150 and 2000 Oe at 4.85 K, B increases almost linearly with H independent of rate, in both magnetization and hysteretic runs.[10]

Note, for hysteretic runs at 7.1 K in the field region where only cooling was observed (30–150 Oe and $dH/dt = 178$ Oe/s), we have found that both the temperature decrease and the magnetic-flux density B are approximately proportional to the square of the applied field.

IV. DISCUSSION

The lack of an observable cooling effect in the magnetization state is most likely the result of a large irreversible heating due to irreversible flux entrance into the sample. Comparison of the two curves in Fig. 2 shows that at the same field, the magnitude of heating in the magnetization run is twice as large as the observed cooling in the hysteretic run and thus would mask most of the cooling effect even if it were present.

We have no complete explanation of the disappearance of the cooling phenomenon below 6.5 K in the hysteretic runs. However, a comparison with data taken at 4.85 K for magnetization runs clearly shows a larger amount of heating for a particular field at lower temperatures.

The disappearance of reversible magnetocaloric cooling below a threshold temperature (2.05 K) has been observed by Burgemeister and Dokoupil[14] when studying the magnetothermal effects of pure niobium. These studies attribute the disappearance of cooling below a threshold temperature to increased entropy production, caused by irreversible flux entrance, at lower temperatures.

We have modeled the observed heating and cooling data for increasing and decreasing applied fields, assuming that it consists of a reversible and irreversible component. In this model, we have assumed that the irreversible component at a given H and dH/dt is the same for both increasing and decreasing applied fields. The results of this model indicate that the irreversible and reversible portions are of comparable magnitude at $H \approx 265$ Oe. Results also show that for increasing applied fields, the reversible cooling would be two to three times larger than the observed cooling at $H \approx 195$ Oe. However, we have no independent experimental confirmation of this model or its predictions.

The results for the magnetocaloric cooling observed here have been modeled using well established principles of thermodynamic phase transitions described by Shoenberg[15] for type-I superconductors. For any type-I superconductor below its transition temperature the full normal state can be returned by the application of a magnetic field greater than H_c. One can calculate the entropy difference between the phases, namely,

$$S_n - S_s = \frac{-H_c(T)}{4\pi} \frac{dH_c(T)}{dT} , \tag{1}$$

where S_n and S_s are the entropies per unit volume in the normal and superconducting state. The value of dH_c/dT is always negative or zero making $S_n - S_s > 0$. The destruction of the superconducting state will result in a decrease in temperature for an adiabatic environment. For a reversible type-II superconductor Eq. (1) will hold with H_c being the thermodynamic critical field. We will assume the usual temperature dependence of H_c, namely,

$$H_c(T) = H_{c0}(1-t^2) , \tag{2}$$

where H_{c0} is the thermodynamic critical field at $T=0$ and t is the reduced temperature T/T_c. Substitution into (1) gives

$$\Delta S_{n/s} = \frac{1}{2\pi} H_{c0}^2 (1-t^2) \frac{t}{T_c} . \tag{3}$$

To evaluate Eq. (3) we must recast H_{c0} in terms of an experimentally measurable parameter. The simplest manner to proceed is to use the Rutger's relation that, at T_c,

$$\Delta C_{n/s}(T_c) = -\frac{1}{4\pi} T_c \left[\frac{dH_c}{dT} \right]^2 , \tag{4}$$

where $\Delta C_{n/s} = C_n - C_s$ is the change in specific heat per unit volume at T_c. Values for $\Delta C_{n/s}/T_c$ ranging from -26 to 67 mJ/f.u. mol K^2 have been reported in the literature for these materials[12,13] and have been converted using our measured value of density (5.43 g/cm^3). Thus, the decrease in temperature for an adiabatic type-II superconductor in an applied field greater than H_{c1} is given by

$$\Delta T = F(1-t^2)t^2 \frac{\Delta C_{n/s}}{2C(T)} T_c , \tag{5}$$

where F represents the fractional amount of material that has returned to the normal state or whose entropy has increased to nearly that of the normal state. In Eq. (5) we have assumed that $\Delta T/T$ is sufficiently small so that the experimentally determined $C(T) \approx$ const. Using Eq. (5), we find that at 7.1 K and $H \sim 100$ Oe the observed ΔT (~ 0.11 mK) gives an F of 0.001–0.0045 %.

If we assume a simple triangular flux lattice for this material, then the vortex lattice parameter is given by $a = 1.075(\Phi_0/B)^{1/2}$ where $\Phi_0 = 2.07 \times 10^{-7}$ G cm^2. The area per vortex unit cell will be $a^2 = A_v = 1.00\Phi_0/B$. We will denote the area of the "quasinormal" state material contained within each vortex unit cell as $A_n = \pi r^2$, where r is the radius over which an appreciable entropy change from the superconducting state extends. In this simplistic model the ratio A_n/A_v represents the fractional amount of normal state material contained within each vortex unit cell and is given by

$$F = \frac{A_n}{A_v} = \frac{\pi r^2}{1.00\Phi_0/\gamma H^2} , \tag{6}$$

where we have substituted the experimental form of $B = \gamma H^2$ for the 30–150-Oe field region. Using this flux lattice model we find that $F \propto \Delta T \propto H^2$, which is consistent with the experimental data in the region where cooling was observed (see Fig. 2). By substituting in the appropriate values into Eq. (6), the radius over which an appreciable entropy change extends was found to be $\sim 50 \pm 20$ Å. The flux lattice model applied to our experimental data implies that an appreciable entropy change extends over an area about the size of a normal core (where the normal core diameter is of the order of the coherence length $\xi \sim 5$–30 Å).[16] Note, the largest source of error in calculating this radius (r) is due to the wide range of values for $\Delta C_{n/s}/T_c$ reported in the literature.

De Gennes,[17] however, has calculated the line energy of an isolated vortex and found that the spatial extent over which an appreciable energy exists is of the order of the penetration depth λ (1400–7000 Å),[18,19] and not ξ. He has also provided an expression for the Gibbs energy of a single vortex; however, we are unable to calculate its temperature dependence (which would yield the entropy) because an accurate temperature dependence of the variables involves in this expression $[B(T), H_{c1}(T), \lambda(T)]$ (Refs. 20 and 21) are not well known for these materials at $T \ll T_c$.

As a final note, using reversible thermodynamics,[22] we have calculated the change in magnetization with respect to temperature

$$\left[\frac{\partial M}{\partial T} \right]_{H,P} = -\frac{C_v}{T} \frac{dT}{dH} \tag{7}$$

at 7.1 K (with $H = 100$ Oe) and found that the calculated value is an order of magnitude smaller than the sensitivity of our measurement (~ 0.1 emu/cm^3 K).

Summarizing the results from our experiment, we find that only heating occurs below 6.5 K. For hysteretic runs at 6.5 and 7.1 K we find both B and ΔT (cooling) $\propto H^2$ in the 30–150-Oe field region. Using a simple flux lattice model, a $B \propto H^2$ leads to a cooling $\Delta T \propto H^2$, which is consistent with the experimental data. We find that an appreciable entropy change occurs over an area about that of a normal core ($\sim \xi$).

ACKNOWLEDGMENTS

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