# Magnetocaloric Effects in $YBa_2Cu_3O_{7-\delta}$: Evidence for a Surface Barrier

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We have found the magnetocaloric effect in $YBa_2Cu_3O_{7-\delta}$ polycrystals in which, for increasing and decreasing magnetic fields applied parallel to the plane surfaces in the range from 0 to 10 T, a pulsed heat evolution, $\Delta Q$, occurs repeatedly at a nearly constant field interval, $\Delta H$, below 30 K. Then, $\Delta H$ decreases very gradually with magnetic field, $-\Delta Q/\Delta H$ is nearly equal to the magnetization, and $\Delta H$ is almost temperature independent. These results indicate that a surface barrier exists against the entry and exit of flux lines, where $\Delta H$ is a measure of the magnitude of the surface barrier.

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Magnetocaloric effects, in which heat is released while the magnetic field is increased or decreased, have been observed in conventional type-II superconductors [1,2]. In high-$T_c$ superconductors, however, because of the very large values of the Ginzburg-Landau parameter and the thermodynamic critical field, we can expect to have a much larger magnetocaloric effect than in conventional type-II superconductors, so that more quantitative and reliable studies become possible.

In this Letter, we report the first observation of magnetocaloric effects in the high-$T_c$ superconductors. It has been found in $YBa_2Cu_3O_{7-\delta}$ polycrystals below 30 K that, during the linear application or removal of an external magnetic field, $H$, parallel to the plane surfaces, a pulsed heat evolution, $\Delta Q$, occurs repeatedly at a nearly constant field interval, $\Delta H$. We have measured $\Delta Q$ and $\Delta H$ as functions of $H$, and $\Delta H$ as a function of temperature. We consider that this pulsed heat evolution indicates the existence of a surface barrier against the entry and exit of flux lines, where $\Delta H$ is a measure of the magnitude of the surface barrier. The existence of this surface barrier was theoretically predicted by Bean and Livingston [3] and by de Gennes [4] for the case of $B=0$, where $B$ is the magnetic flux density, and further developed by Ternovskii and Shekhata [5] and by Clem [6] for the case of $B\neq 0$.

It has often been observed in high-$T_c$ superconductors that the first field for flux penetration, $H_p$, rises strongly with decreasing temperature. McElfresh *et al.* have considered that the low-temperature increase in $H_p$ is due to the surface barrier [7], where they are concerned only with the surface barrier for $B=0$. However, we interpret the present magnetocaloric results as showing that, even for $B\neq 0$, the surface barrier exists not only for the flux entry in increasing field, but also for the flux exit in decreasing field in the wide field range of up to 10 T, the maximum field we used. Then, $\Delta H$ decreases gradually with increasing $H$, which is consistent with theoretical predictions [5,6].

Other results we obtained are as follows: (i) $\Delta Q$ is nearly equal to $-M\times\Delta H$, where $M$ is the magnetization. Namely, the heat evolution corresponds to the work done in the superconductive bulk by the flux lines which are driven by the external magnetic field. (ii) $\Delta H$ is almost temperature independent below 30 K, which shows that the flux entry is not a thermally activated process. This is in contrast to the low-temperature increase of $H_p$ mentioned above. Then, the experimental value of $\Delta H$ is much less than the theoretical one [4]. Both the temperature independence and the smallness of the experimental $\Delta H$ value suggest the possibility of quantum tunneling of flux lines through the surface barrier.

The calorimeter used is a conventional adiabatic one with a mechanical heat switch. Evolved heat was calculated from the temperature rise measured adiabatically and the predetermined heat capacity of samples and addenda. The heat capacity was measured using a standard heat-pulse method. The heat switch allowed one to adjust the heat leak from the samples to the surroundings and the measure $\Delta H$ with the temperature rise suppressed. The preparation of the polycrystalline $YBa_2Cu_3O_{7-\delta}$ samples was carried out according to a standard ceramic technique and the superconducting transition temperature $T_c$ was 91.5 K. One set of samples used for measurements consisted of 14 pieces of flat plates of $17\times 10\times 1.2$ mm$^3$. One side of each of the stacked plates was bonded to a sapphire thin plate, which was equipped with a carbon-glass resistance thermometer, a platinum resistance thermometer, and a constantan heater. The magnetic field was applied parallel to the large plane surfaces. The demagnetizing factor was estimated to be about 0.09 using an ellipsoidal approximation. Unless otherwise stated, however, the field was not corrected for the demagnetizing effect. The temperature of the samples was recorded while the magnetic field was increased or decreased linearly in time. The sweep rate ranged from 0.1 to 1 mT/s. As to the specific heat, $C$, of the samples, the $C/T$ upturn at $H=0$ and the Schottky-like anomalies at $H\neq 0$ were observed at low temperatures. Fitting the $C/T$ vs $T^2$ curve for $H=0$ by a straight line visually in the temperature range 6–10 K gave the linear term of $\gamma=4.2$ mJ/(mol K$^2$). The specific heat jump at $T_c$, $\Delta C/T_c$, was about 30 mJ/(mol K$^2$), which was estimated by the extrapolation method with the entropy

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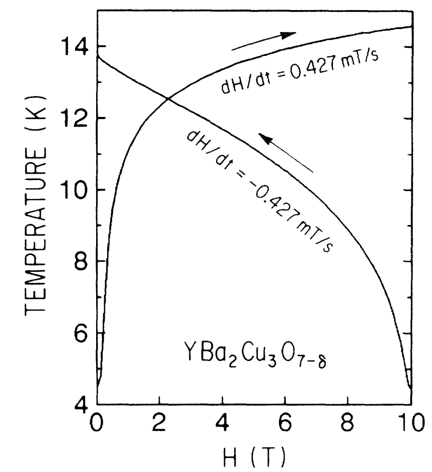


FIG. 1. Temperature change of $YBa_2Cu_3O_{7-\delta}$ polycrystals with the addenda measured adiabatically as a function of increasing and decreasing magnetic field, $H$.

balance.

Figure 1 shows the temperature rise of $YBa_2Cu_3O_{7-\delta}$ samples with the addenda which was measured adiabatically starting from 4.3 K, when the magnetic field parallel to the plane surfaces was increased from 0 to 10 T and decreased from 10 to 0 T at the sweep rate of $dH/dt = \pm 0.427$ mT/s. Apparently, the temperature seems to rise continuously as a function of $H$. However, if the scale is enlarged, the curves show that the temperature of samples rises stepwise. In other words, the pulsed heat evolution occurs repeatedly at a nearly constant interval during the linear application or removal of the magnetic field.

Figure 2 shows the integrated heat evolution as a function of increasing magnetic field from $H_0$ to $H_0+0.1$ T at $dH/dt=0.240$ mT/s. The temperature of the samples is between 4.3 and 6.8 K. For clarity, the density of data points plotted in the figure is reduced to $\frac{1}{5}$ of that of the measured ones. At the start of each run, the samples are in a thermal equilibrium state at a temperature of around 4.3 K and the magnetic field is $H_0$. No heat evolution can occur until the magnetic field is changed by the step $\Delta H$. When it is changed by $\Delta H$, the heat evolution of $\Delta Q$ occurs instantaneously. Then, no heat evolution follows until the next field change of $\Delta H$. As is shown later, the heat evolution corresponds to the work done by the movement of the flux lines, which is caused by the external magnetic field. Thus, this pulsed heat evolution indicates that, even if $H$ is increased above the lower critical field, the flux lines do not enter continuously, and their entry is delayed by $\Delta H$.

In each run, the initially measured value of $\Delta H$ is larger than the succeedingly measured ones. Perhaps, the reason is that it takes some time for the system of samples and addenda to reach a kind of thermally steady state. So, in the following analysis of $\Delta H$, we will not

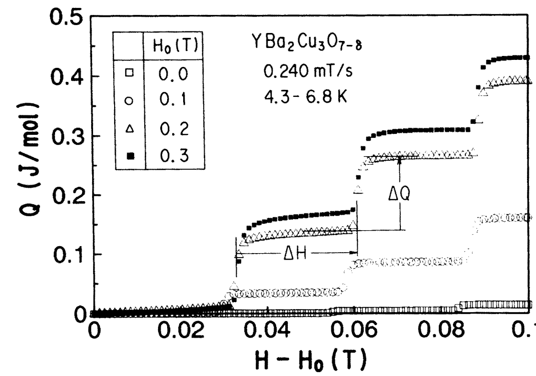


FIG. 2. Integrated heat evolution, $Q$, in $YBa_2Cu_3O_{7-\delta}$ as a function of increasing magnetic field, $H-H_0$, where $H_0$ is the starting magnetic field. Pulsed heat evolution of $\Delta Q$ occurs at every field increase of $\Delta H$. For clarity, only $\frac{1}{5}$ of measured data points are plotted.

consider the initially measured value. In Fig. 2, at $H_0=0$, the initial heat evolution is detectable at about 54 mT. Namely, $H_p$ at 4.3 K is about 54 mT, although it may be overestimated due to the above-mentioned time lag.

Figure 3 shows $\Delta H$ as a function of $H$. The open and solid circles are the data for increasing and decreasing fields of 0.427 mT/s, respectively. The temperature was held between 4.24 and 4.9 K using the heat switch. The data in Fig. 1, which were measured adiabatically in a much wider temperature range, also give almost the same relation of $\Delta H$ vs $H$ as in Fig. 3. All of the data show that $\Delta H$ decreases with the magnetic field from 26 to 27 mT at $H \simeq 0.1$ T to about 22 mT at $H \simeq 10$ T.

The present pulsed heat evolution indicates clearly that a surface barrier exists against both the flux entry in increasing fields and the flux exit in decreasing fields in the wide range of magnetic fields of $H=0$–10 T, where $\Delta H$ is a measure of the magnitude of the surface barrier [3-6]. The decrease of $\Delta H$ with the magnetic field is consistent

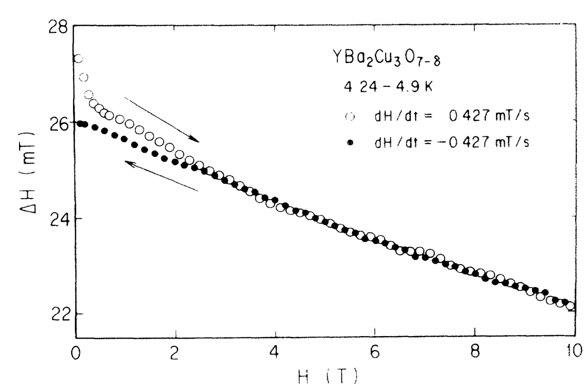


FIG. 3. Field interval, $\Delta H$, for pulsed heat evolutions in $YBa_2Cu_3O_{7-\delta}$ as a function of increasing and decreasing magnetic field, $H$.

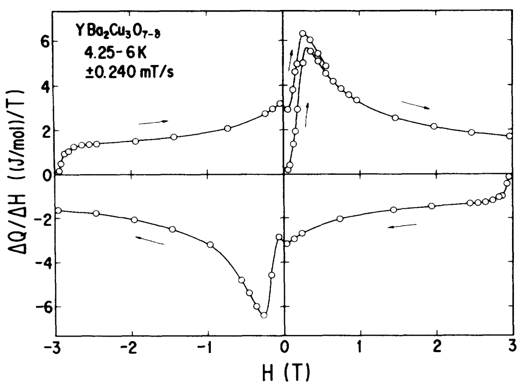


FIG. 4. $\Delta Q/\Delta H$ vs $H$ in $YBa_2Cu_3O_{7-\delta}$.

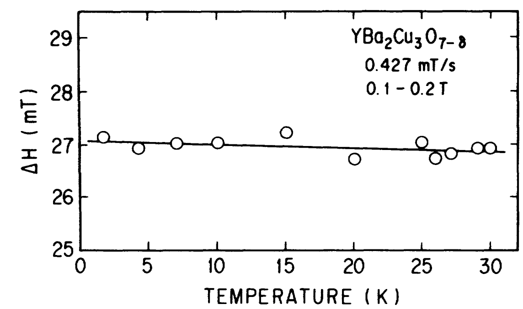


FIG. 5. Temperature dependence of $\Delta H$ in $YBa_2Cu_3O_{7-\delta}$.

with the theoretical prediction [5,6], in which the entry barrier is a monotonically decreasing function of $B$ for $\phi_0/\lambda^2 \ll B \ll \phi_0/\xi^2$, where $\phi_0$, $\lambda$, and $\xi$ are the flux quantum, the penetration depth, and the coherence length, respectively. In Fig. 3 the barrier to flux entry is nearly of the same magnitude as the barrier to flux exit as compared at the same magnetic field. Incidentally, in conventional type-II superconductors, the existence of the surface barrier has been confirmed by the measurements of flux entry and exit, and the $\Delta H$ vs $H$ curves similar to Fig. 3 have been observed [8-10].

Figure 4 shows $\Delta Q/\Delta H$ as a function of $H$ for $dH/dt = \pm 0.240$ mT/s, where the temperature range used for the measurement is between 4.25 and 6 K. It should be noted here that in the calorimetry the constant temperature can be achieved only approximately because a small temperature rise is inevitably needed for measurement of released heat. The $\Delta Q/\Delta H$ vs $H$ curve shows the same hysteresis as the $-M$ vs $H$ curve observed in typical type-II superconductors, where $M$ is the magnetization.

We measured the magnetization on one of the samples used for the calorimetry, whose size was $3.9\times5.6\times1.2$ mm$^3$, at 5 K with the magnetic field parallel to large plane surfaces. For the initial magnetization, the magnitude of $\Delta Q/\Delta H$ was considerably smaller than that of $-M$. Except for the initial magnetization, however, $-M/(\Delta Q/\Delta H)$ was $0.89\pm0.01$. Hence, if we take account of the difference in principle, sample size, and time schedule between the two measurements, we may conclude that $\Delta Q$ is nearly equal to $-M\times\Delta H$. In other words, the heat evolution is due to the work done in the superconductive bulk by the external field and is not related to the weak links between the grains.

The hysteresis of magnetization has been explained by the critical state model, which was proposed by Bean [11]. In the model, the distribution of magnetic flux density within a sample is determined by the pinning of flux lines at some lattice defects. However, the pulsed heat evolution suggests that this pinning effect on the motion of flux lines may be much weaker than the effect of surface barrier on their motion [9]. The evolved heat is the difference in energy between the initial and the final distribution of flux lines, and is independent of their intermediate pinning and depinning. Thus, once the flux lines enter or exit out of the samples through the surface barrier, a new critical state will be instantaneously achieved with the heat evolution and again the surface barrier will be formed against the next entry or exit of flux lines.

Figure 5 shows $\Delta H$ as a function of temperature, which was measured in the field range from 0.1 to 0.2 T at the increasing field of 0.427 mT/s. In the temperature range from 1.5 to 30 K, $\Delta H$ is almost temperature independent. This shows that flux entry is not a thermally activated process. Above 30 K, it was difficult to observe the temperature rise due to heat evolution because of the large heat capacity of samples and addenda.

The theory of the surface barrier for $B=0$ [3,4] shows the following: When $H < H_{c1}$, the force on the flux line always points towards the surface, where $H_{c1}$ is the lower critical field. When $H_{c1} < H < H_s$, there is a surface barrier opposing the entry of flux lines, although their entry is thermodynamically allowed. When $H > H_s$, the barrier disappears. Here, $H_s$ is the theoretical surface barrier field to flux entry for $B=0$. For $\kappa \gg 1$ it has been found that $H_s = H_c$ exactly [4], where $\kappa$ $(=\lambda/\xi)$ and $H_c$ are the Ginzburg-Landau parameter and the thermodynamic critical field, respectively.

The thermodynamic critical field at zero temperature has been estimated to be $H_c(0) = 1.23\pm0.13$ T [12-14]. Therefore, $H_s$ for $B=0$ at zero temperature is about 1.23 T, which is compared with the experimental $\Delta H$ value for $B\simeq0$ at about 4.5 K. The experimental $\Delta H$ is about 27.3 mT. If corrected for the demagnetizing factor, it is about 30 mT. Namely, the experimental $\Delta H$ is much less than the theoretical $H_s$; $\Delta H$ is only about $\frac{1}{40}$ of $H_s$. Surface irregularities such as surface convexities may cause local field concentrations along the surface and hence serve as centers for the entry of flux lines in an increasing field [3,15]. In a decreasing field, these same field concentrations will oppose the exit of flux lines, and other spots such as surface concavities may produce lowered local surface fields that may encourage flux exit [3]. The mere fact of such a field concentration or lowering, however, seems to be insufficient to explain the large difference between $H_s$ and $\Delta H$.

There is another possible explanation for this difference. The lower critical field $H_{c1}^{ab}$ at zero temperature for the field parallel to the *ab* plane has been estimated to be $120 \pm 10$ Oe [16], $180 \pm 20$ Oe [17], 70 Oe [18], or 110 Oe [19]. Therefore, the experimental $\Delta H$ for $B \simeq 0$ is roughly $3H_{c1}^{ab}$. In the case of flux entry, the above theory [3,4] shows that the width of surface barrier for $H \simeq 3H_{c1}$ is about $\frac{1}{3}$ of the penetration depth if we take either $\kappa^{ab} = 370$ or $\kappa^{c} = 52$ [12,19]. We may speculate that in the case of superconductors with $\kappa \gg 1$ the flux lines could penetrate through such a surface barrier by quantum tunneling [20]. If the local fields are concentrated at surface irregularities, then the width of the surface barrier may be much thinner for the same $H$, and quantum tunneling of flux lines is more likely to occur. Once the first flux line tunnels through the surface barrier, the released energy may enhance the tunneling of successive flux lines, resulting in the present pulsed heat evolution. Hence, we consider the temperature independence and smallness of $\Delta H$ as suggesting the possibility of quantum tunneling of flux lines through the surface barrier. Incidentally, a temperature-independent magnetic relaxation has been found in $YBa_2Cu_3O_{7-\delta}$ below 1 K, and interpreted as showing the existence of quantum tunneling of flux lines [21,22].

In summary, we have observed the magnetocaloric effect in $YBa_2Cu_3O_{7-\delta}$ polycrystals in which the pulsed heat evolution occurs repeatedly for increasing and decreasing magnetic fields in the range from 0 to 10 T at a nearly constant field interval below 30 K. This indicates that a surface barrier exists against the entry and exit of flux lines. The possibility of quantum tunneling of flux lines through the surface barrier is suggested. It would be highly desirable to study the magnetocaloric effects in single crystals in order to make the mechanism clearer.

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