Memory Effects in a Superconducting Y-Ba-Cu-O Single Crystal: A Similarity to Spin-Glasses

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We report on memory effects observed in the time dependence of the magnetization $M(T,H)$ of a superconducting Y-Ba-Cu-O single crystal. As in spin-glasses, the decay rate $S = dM/d\ln t$ is not uniquely determined. It exhibits a characteristic change at time t equal to the waiting time t_w during which the specimen was kept at a given temperature $T < T_c$ and magnetic field H before a field perturbation ΔH is applied at time $t=0$. This phenomenon, seen for the first time in a superconductor, reveals the glassy nature of the superconducting state in the high-T_c oxides.

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Since the original work of Müller, Takashige, and Bednorz[1] and their observation of glasslike properties in the high-T_c superconducting oxides, much effort has been made to verify the existence of a superconducting-glass state in these materials. It was suggested that the glass state originates from the anomalously small coherence length ξ found in the oxides,[2] which favors the creation of a network of weak links at grain boundaries in ceramics, and at twin boundaries in single crystals.[3] Recent experiments have shown that the critical current density J_c in ceramics and powdered single crystals Y-Ba-Cu-O is independent of the grain size, leading to the conclusion that weak links within grains play a major role.[4] Theoretical models[5] and numerical simulations[6] for superconducting glass can successfully reproduce the main observable properties (both equilibrium and nonequilibrium) of the high-T_c superconductors and predict a phase diagram in the H-T plane. There are at present a number of experimental studies[7,8] including the muon-spin rotation method[9] on the difference between field-cooled (FC) and zero-field-cooled (ZFC) magnetic measurements, and on the existence of the "quasi de Almeida-Thouless" or irreversibility line. The long-time nonexponential relaxation behavior of the magnetization M has been reported on ceramics,[10,11] single crystals,[12,13] and thin films.[14] Some authors used the observed logarithmic time decay of M, and the specific temperature and field dependence of the decay rate $S = dM/d\ln t$ as an argument in favor of a glass picture. Recently, Yeshurun and Malozemoff[13] proposed the existence of giant flux creep in these materials as an alternative to the superconducting-glass model.

We report here for the first time a direct observation of aging and memory effects in a single crystal of a 90-K superconductor $Y_1Ba_2Cu_3O_{7-\delta}$, a prominent feature found up to now only in spin-glasses such as CuMn, studied in detail by Lundgren and co-workers,[15,16] and described by a recent theory of Koper and Hilhorst.[17] Our results based on a systematic study of the time decay of the magnetization below T_c are strong evidence that high-T_c superconductors can be described by a glass picture. In fact the superconducting-glass theory[6] contains the basic elements of spin-glass theory, i.e., a hierarchy of free-energy barriers leading to a broad distribution of relaxation times τ probably associated with the presence of frustrated superconducting domains coupled by weak links.

A single-crystal platelet of $1.8 \times 1.2 \times 0.08$ mm^3 ($m = 1.12$ mg) with c axis perpendicular to its plane, was mounted on a sapphire sample holder. A SHE SQUID magnetometer was used for the measurements, with the magnetic field applied parallel to the c axis. The magnetization of the sample holder was calibrated in all relevant experimental conditions. The holder signal was always much smaller than the sample contribution. Long-time (up to one day) temperature and field stabili-

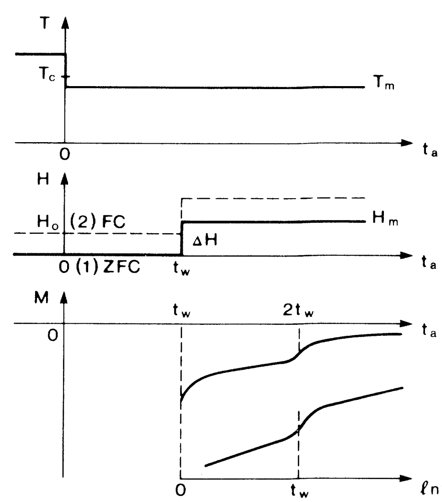

FIG. 1. Experimental procedure for measurement of the time decay of the magnetization M of a superconductor (1) zero field cooled (ZFC) or (2) field cooled (FC) to a temperature $T_m < T_c$ at time $t_a = 0$. The aging time of the system is $t_a = t_w + t$ where t_w is the waiting time and t is the actual measuring time of the relaxation after the application a field step ΔH. On a logarithmic time scale M shows a characteristic inflection point at $t = t_w$.

ties of the setup were also carefully checked. The experimental procedure is summarized in Fig. 1. As soon as the sample is stabilized at its measuring temperature T_m after the ZFC or FC process through T_c, the aging time t_a of the system is measured. The system is then left in its quasiequilibrium state (T_m, H_0) for a certain waiting time t_w before the applied magnetic field is increased by ΔH to the measuring field H_m. Just at this time we start measuring the relaxation of the trapped magnetic flux. The measuring time t is related to the total aging time t_a by $t_a = t_w + t$. The change in the decay rate at $t \approx t_w$ (or $t_a \approx 2t_w$) appearing as an inflection point in the M vs $\ln t$ plot is the signature of the memory effect as explained below.

The temperature dependence of the decay rate $S = dM/d\ln t$ is plotted in the inset of Fig. 2 for the ZFC Y-Ba-Cu-O single crystal. The measurements were started immediately after application of a field of 1 kOe with $t_w = 0$. We have observed that the deviation from a $\ln t$ behavior becomes significant at larger field or at temperatures close to T_c. The rate S increases with T up to a maximum at about 30 K before decreasing progressively as T_c is approached. This behavior was reported by several groups[11-14] and explained in some cases by thermally activated flux creep.[18] From the analysis of their data, Yeshurun and Malozemoff[13] found unusually small pinning energies ($\lesssim 0.1$ eV) in Y-Ba-Cu-O. These values, about 1 order of magnitude smaller than those in conventional superconductors, suggested to them the term "giant" flux creep.

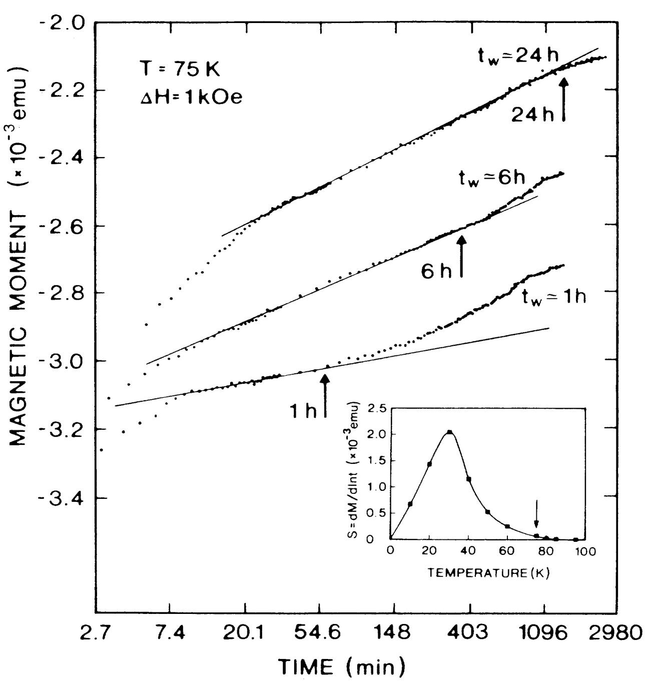

FIG. 2. Magnetic moment M vs $\ln t$ of the ZFC Y-Ba-Cu-O single crystal. The sample was maintained at 75 K within the remanent field of the superconducting coil for the different waiting times $t_w = 1$, 6, and 24 h, before application of a field step ΔH of 1 kOe. For clarity, the data points for $t_w = 24$ and 1 h have been shifted up and down by 4×10^{-4} and 6×10^{-4} emu, respectively. Inset: The temperature dependence of the decay rate $dM/d\ln t$ (t in sec) measured in the ZFC single crystal after application of a field of 1 kOe without waiting ($t_w = 0$). The solid line is a guide to the eye. The arrows indicate the temperature at which the aging effect is observed.

In Fig. 2 the decay of the magnetization M of the ZFC single crystal is displayed on a logarithmic time scale for three different waiting times t_w at $T = 75$ K ($T/T_c = 0.8$) and with $\Delta H = 1$ kOe. In reality, the starting field H_0 is not zero but is the small remanent field of the superconducting magnet (≤ 30 Oe). After an initial transient response ($t < 10$–20 min) M decays logarithmically in time. However, the decay clearly deviates from $\ln t$ at a measuring time t equivalent to the waiting time t_w (see arrows in Fig. 2). Such echolike responses to a field jump applied at $t = 0$ were observed in spin-glasses.[15-17]

Our letting the system evolve in a field $H_0 \gtrsim 0$ does not seem optimally suited for observing the memory effect. A field $H > H_{c1}$ generating frustration in the superconductor is needed to produce a large hierarchy of relaxation processes. By our cooling the sample in larger fields, for example, $H_0 = 0.5$ kOe, a sharper change in the decay of $M(t)$ occurs around t_w, as seen in Fig. 3. In that case, the waiting time t_w was increased from 98 min up to 360 min. The magnitude of the $M(t)$ jump is about 50 times larger than any fluctuations in the sample-holder signal. The fact that this jump does not always occur at $t = t_w$ is most likely due to some irreproducibility in the preparation of the initial state (T_m, H_m) at $t = 0$. In addition to the importance of the magnitude of

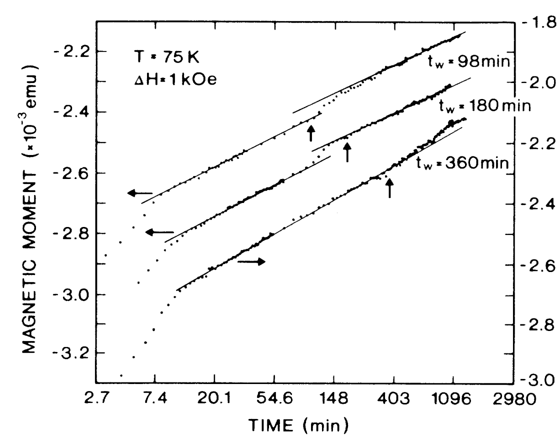

FIG. 3. Magnetic moment M vs $\ln t$ of the Y-Ba-Cu-O single crystal cooled to 75 K in a field $H_0 = 0.5$ kOe, measured upon application of a field step ΔH of 1 kOe after three different waiting times $t_w = 98$, 180, and 360 min (indicated by vertical arrows).

H_0, the amplitude of ΔH is also critical. If ΔH is either too small or too large, the characteristic memory feature in M vs $\ln t$ disappears. This point was checked by measurement of the decay of $M(t)$ in the FC state ($H_0=0.5$ kOe) after application of different field steps ΔH ranging from 0.5 to 1.5 kOe, and by our waiting about 1 h. The inflection point in $M(t)$ is visible only for ΔH around 0.75 to 1.0 kOe. This is in qualitative agreement with the H-T phase diagram proposed by Morgenstern, Müller, and Bednorz,[6] in which the irreversible superconducting-glass state narrows considerably in fields close to T_c. The memory effect is likely to be seen only in the temperature range where the FC relaxation of M is larger, typically for $0.7 \lesssim T/T_c \lesssim 0.9$.[13]

To discuss the role of the magnetic field, we first describe a model that we believe applies to high-T_c superconductors. The effect of H_0 on the network of weak links in the specimen is to produce frustration. This leads to a hierarchy of barriers similar to the free-energy landscape in spin-glasses which corresponds to a broad distribution of relaxation times.[19] This distribution $g_H(\tau)$ vanishes above some $\tau_{\max}$. Since the number of relaxation processes which remain active decreases during the aging, a time-dependent density of those processes can be defined by $D(\tau,t_a,H)=g_H(\tau)\exp(-t_a/\tau)$.

The net magnetization measured at $t_a > t_w$ has the form $M(t_a)=M_{\rm eq}+\Delta M(t_a)$, where $M_{\rm eq}=\lim_{t\to\infty}M(t_a)$ is the equilibrium magnetization. The excess magnetization $\Delta M(t_a)$ is defined by $\Delta M(t_a)=\chi\Delta H R(t_a,t_w)$, with χ the diamagnetic susceptibility and $R(t_a,t_w)$ a response function to the field step ΔH. This response term has the form

$$R(t_a,t_w)=\frac{\int_0^{\tau_{\max}}D(\tau,t_a,H_m)\,d\tau}{\int_0^{\tau_{\max}}D(\tau,t_w,H_m)\,d\tau},$$

and satisfies the condition $R=0$ in the limit $t\to\infty$. The relaxation of M is therefore governed by the response function R which includes the evolution of the density $D(\tau,t_a,H_m)$ during aging. The evolution of D on a logarithmic time scale is schematically described in Fig. 4. At $t_a=0$, the initial distribution induced by H_0 has a given shape $D_1(\tau,0,H_0)$ but is drawn for simplicity as a horizontal line in Fig. 4 (curve 1). As the FC sample ($H_0>0$) is left to itself during t_w, it slowly ages and D_1 evolves towards $D_1(\tau,t_a=t_w,H_0)$ (curve 2) by relaxation of all the short-time processes with $\tau < t_w$. The effect of ΔH at $t_a=t_w$ is to create a second distribution $D_2(\tau,t_a=t_w,H_m=H_0+\Delta H)$ (curve 3) which is added to D_1, leading to $D(\tau,t_w,H_m)=D_1+D_2$ (curve 4). We assume here that the principle of superposition is valid as in spin-glasses.[16] D governs the relaxation of M effectively measured in the experiment, and evolves for $t_a \gtrsim t_w$, towards $D(\tau,2t_w,H_m)$ (curve 5) by losing its short-time components. During all that time the large τ components of the old distribution D_1 are active but on a logarithmic time scale their effect is relatively small. This is shown by the dashed line 5 in Fig. 4. At that point ($t_a \simeq 2t_w$), it is clear from the expression for the response function R that a change in the decay rate of M occurs and leads to the M vs $\ln t$ inflection point. The field step ΔH is therefore needed to probe the age of the system and produce the echolike feature. The memory effect manifests itself by the following: (a) a change of slope in the M vs $\ln t$ curve, and (b) a jump in M, both at $t_a \simeq 2t_w$. In spin-glasses the amplitude of the jump at $2t_w$ decreases with increasing waiting time (see Ref. 15). This possibly explains the absence of jump in the $t_w=24$-h data of Fig. 2.

In summary, the following conditions are expected to be important for observation of the aging process: (1) A basic magnetic field H_0 is needed in order to create a broad distribution of barriers; (2) The field step ΔH must have an amplitude large enough to superimpose a new barrier landscape but small enough not to destroy the initial landscape and wash out the "memory" of the magnetic-flux state; (3) The temperature has to be high enough for the system to experience the hierarchy of barriers, since at low temperature it would be restricted to only a few barriers during observation time.

Up to now we have defined the exact nature of the processes which lead to the aging of the superconducting glass mainly because of the complicated nature of the oxides. Twin boundaries, dislocations, point defects, and oxygen disorder are some of the possible contributors. Superconducting-glass scenarios based on disorder and frustration[5,6,20] invoke changes in the magnetic configuration of the system through nucleation and diffusion of flux lines within the network of weak links. As the specimen is field cooled, the superconducting regions are initially out of equilibrium. Slowly, equilibrium builds up

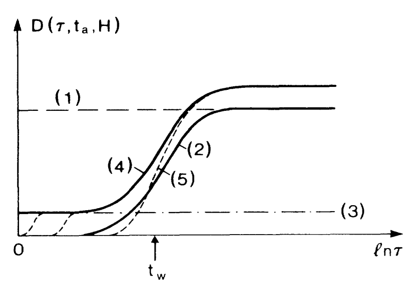

FIG. 4. Time evolution of the density of relaxation processes $D(\tau,t_a,H)$ in a FC superconducting glass. Curve 1 is $D_1(\tau,t_a=0,H_0)$ plotted as a constant for simplicity. During the waiting time t_w it evolves towards $D_1(\tau,t_w,H_0)$ (curve 2). The field step ΔH creates a new distribution $D_2(\tau,t_w,H_m=H_0+\Delta H)$ (curve 3) which is added to D_1 and yields

$$D(\tau,t_w,H_m)=D_1(\tau,t_w,H_M)+D_2(\tau,t_w,H_m)$$

(curve 4). Relaxation of the short-time components ($\tau < t_w$) of D leads to $D(\tau,2t_w,H_m)$ (curve 5).

between these regions, forming domains of correlation. As the size of these domains increases with aging time, supercurrents can flow over larger areas and improve the screening against H_0. In fact, the net diamagnetic moment measured in this situation rises slowly with time, but at a rate about a thousand times less than that after ΔH has been turned on. For $t_a > t_w$ the domains incorporate additional flux lines generated by ΔH. The induced relaxation process then leads to the memory effect. Therefore, the physical picture of the aging process is similar to the growth of domains of correlated spins postulated by the theory for spin-glasses.[17]

In conclusion, the aging experiment supports the conjecture originating in the glass theory which states that, in the high-T_c superconductors, typical glass features are to be found at temperatures close to T_c, and for longer observation times. It cannot be explained by a standard or giant flux-creep model which may be considered only as the particular limit of the glass picture for low temperatures and shorter observation times.[21] In fact, the giant flux-creep model proposed initially[13] had to be extended to include a distribution of pinning barriers in order to account for the "puzzling" properties at higher temperatures.[22]

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