Strong magnetic relaxation toward diamagnetism and evidence for glassy behavior in $YBa_2Cu_3O_{7-\delta}$ single crystals close to T_c

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Magnetic-relaxation measurements have been performed on $YBa_2Cu_3O_{7-\delta}$ single crystals. In a temperature range of ≈ 2 K below the transition the diamagnetic magnetization *increases* with time. This increase is barely noticeable for more than ten minutes and then develops in a nonlogarithmic manner for hours. Controlled small temperature changes applied during a relaxation run cause sharp magnetization responses that are fully analogous to findings for nonmetallic spin glasses. The effect correlates with a quasihysteretic anomaly in field-cooled magnetization found recently.

Large magnetic relaxation has been observed in all high-T_c superconductors. Such behavior as a consequence of a superconducting glassy state, caused by granularity, was first reported by Müller *et al.*[1] Later similar large relaxations for single crystals were reported by Yeshurun and Malozemoff.[2] They proposed a more conventional "giant flux-creep" model. According to flux-creep theory[3,4] the *decay* of magnetization is logarithmic in time. Recently, several authors[5] have reported on a nonlogarithmic decay of magnetization for high-T_c single crystals. Interpretations use a vortex glass theory[6] or a collective pinning theory.[7]

In a recent paper[8] we have reported on an irreversibility ("quasihysteresis") in the field-cooled (FC) magnetization for $YBa_2Cu_3O_{7-\delta}$ single crystals. Such behavior occurs when the direction of stepwise temperature changes is reversed and yields different onset temperatures to superconductivity for the field-cooled-cooling path ($T_c^{FCC}=92.3$ K) and for both, the field-cooled-warning- and zero-field-cooled paths ($T_c^{ZFC}=T_c^{FCW}=91.7$ K). From the fast reaction of magnetization on small temperature steps within the "quasihysteresis" we proposed the presence of a spin-glass type relaxation process. We have performed direct magnetic relaxation measurements on the same single crystals in a narrow temperature range (≈ 2 K) below $T_c=92.3$ K for fields applied parallel to the *ab* planes. For field ranges 0.5 Oe $\leq H_a \leq 10$ Oe and temperature range 89 K $\leq T \leq 91.8$ K we find a nonlogarithmic *increase* of diamagnetic magnetization, and a characteristic asymmetric response of magnetization on small temperature steps (± 0.1 K). This fully supports the above-mentioned proposal.

The two single crystals used are platelike with the *c* axis normal to the plane and with dimensions approximately 1.1–1.6 mm in the plane of the plate and about 0.1 mm thick. Both crystals have twin boundaries running along both the $<110>$ and $<1\bar{1}0>$ directions. The high quality single crystals with transition widths of $\lesssim 0.5$ K were grown by a self-flux method[9] and postannealed in flowing oxygen. Magnetic relaxation measurements were taken with a commercial SQUID magnetometer (Quantum Design, Inc.), equipped with a 5.5-*T* superconducting magnet. The contribution of the sample holder was found to be time independent and much smaller than the sample contribution. Paramagnetic influences caused by oxygen contamination of the measuring system were negligible. Superconducting magnets show history dependent remanent magnetic fields. Here these fields are of order 1 Oe and always negative if the "no overshoot" mode is used and high fields ($\gtrsim 200$ Oe) have been avoided for several days. To detect polarity and strength of remanent fields we used a high quality Nb sample with nearly the same demagnetization factor and mass as our crystals. Examining the SQUID response curve (three distinct extrema) the remanent field was compensated repeatedly until an estimated remanence of ± 0.05 Oe remained. "Paramagnetic" moments as reported by Blunt *et al.*,[10] caused by a nonuniform magnetic field, can be excluded. Different scan lengths, which would change the field inhomogeneity significantly, have been used. No changes of the time dependent *increase* of magnetization, to be described, were found. To test the field stability shielding (ZFC) measurements on $YBa_2Cu_3O_{7-\delta}$ single crystals and on Nb for temperatures well below T_c were made and yield constant magnetizations ($\Delta M/M < 10^{-4}$) for ≈ 5 h. Therefore the field is to be assumed constant within this limit. Further, and most importantly, thermal drifts specifically to lower temperatures which might induce a time dependent increase of magnetization, are fully excluded by the observation that the general form of the long-term relaxations to be described is completely independent of the thermal history during establishing the constant measuring temperature.

All magnetic relaxation measurements were performed after a preceding ZFC run ($H_{rem} \lesssim 0.05$ Oe). Figure 1(a) displays susceptibility measurements M/H_a for the single crystal *A* (875 μg) at a constant magnetic field $H_a=1$ Oe $\|ab$ and for four temperatures ranging from 90 to 91.8 K. The first magnetization data were taken 10 s after application of the measuring field. Further data are equidistant in $\log(t)$. As for the initial susceptibility, note that only for the lowest temperature $T=90.0$ K this starting

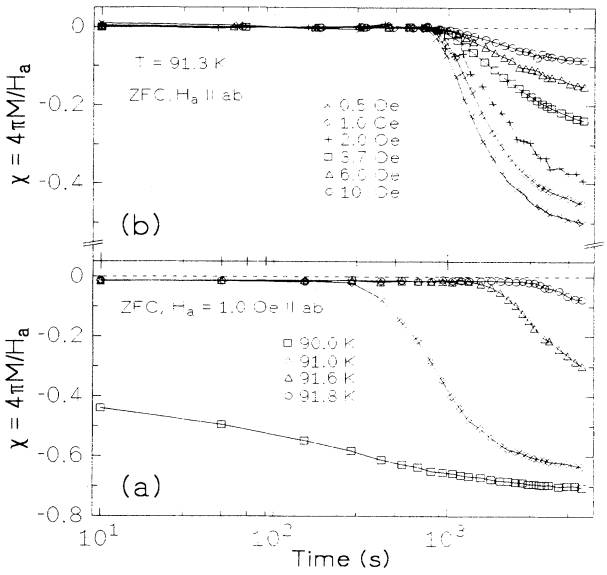

FIG. 1. Relaxation of ZFC susceptibility for single crystal A at (a) constant magnetic field $H_a = 1.0$ Oe at four different temperatures and (b) at constant temperature $T = 91.3$ K at six different fields.

value is large ($4\pi M/H_a \approx -0.44$), while for the higher temperatures it is zero within experimental resolution, including a rest remanence of the magnet. This quasizero susceptibility is practically retained for differing times, ranging from 5 ($T = 91.0$ K) to 50 min (91.8 K). A common feature of all measurements is the strong nonlogarithmic *increase* of susceptibility with time. The steepest slopes of susceptibility occur at times that increase with temperature. For long times the susceptibility tends to saturate but equilibrium is not reached within observation time (6×10^3 s).

In Fig. 1(b) magnetic relaxation measurements are shown for a constant temperature $T = 91.3$ K and for 0.5 Oe $\leq H_a \leq 10$ Oe. The overall picture is similar. The initial susceptibility $\chi(t = 10s)$ for all runs is nearly zero followed by a strong nonlogarithmic *increase* with time. Reproducibility for both types of measurements is outstanding if the starting conditions, viz., H_{rem}, measuring field and temperature, cooling rate, and waiting time, are exactly the same. Crystal B shows nearly identical behavior of susceptibility with time. Incidentally, in a temperature regime 30 K $< T <$ 80 K we observe the well-known nearly logarithmic *decay* of susceptibility with time.[2,5]

For the following grounds we believe that the virtually complete suppression of diamagnetism in the relaxation process cannot be caused by paramagnetic or ferromagnetic impurities. In conventional hysteresis loop measurements of magnetization versus field up to ±50 kOe and at temperatures below 90 K we found no paramagnetic or ferromagnetic moments within experimental resolution. Also in magnetization measurements versus temperature up to 300 K there were no traces of magnetic impurities. Further, inductively coupled plasma-atom emission spectroscopy analysis yielded magnetic impurity concentrations of Fe and Mn below 6 ppm and 0.2 ppm, respectively.

We conclude this part by stating that there is a nonequilibrium state in which diamagnetism is almost fully suppressed. This state is restricted to a temperature regime close to T_c and relaxes nonlogarithmically toward a state which appears to be close to, but not fully, that of a bulk superconductor. The long times, of order of minutes to hours, within which almost no changes in susceptibility seem to occur may be a reason why the effect has escaped attention till now.

Granularity, caused by spatial oxygen deficiencies,[11] possibly leads to a random network of Josephson junctions and including frustration of the phase factors, a superconducting glass state may be introduced.[1,12,13] A possible explanation of the time dependent suppression of diamagnetism might be found in the appearance of spontaneous supercurrents flowing around loops of Josephson junctions with negative Josephson coupling (π junctions).[14] In contrast to other authors[15,16] we have found no indication of a related "paramagnetic Meissner effect." Moreover, zero magnetization seems to be a natural limit for all our relaxation measurements as will be shown below (Fig. 3).

The results presented so far are reminiscent of the relaxation processes found in spin glasses. Indeed, in our interpretation of "quasihysteretic" behavior of stepwise FCW magnetization measurements we have made use of findings for insulating or semiconducting spin glasses.[8] It is natural to look for the action of artificial temperature steps on the relaxation process. Figure 2 displays a ZFC magnetic relaxation measurement for crystal B (370 μg) at $T = 91.6$ K and $H_a = 2$ Oe including three step decreases in temperature, each $\Delta T = -0.1$ K, followed by reversed step increases in temperature, each $\Delta T = +0.1$ K. Also shown is the undisturbed relaxation run for identical history (temperature, magnetic field, cooling rate, and waiting time including the time elapsed between crossing T_c and reaching the measuring temperature). After a temperature step it takes ≈ 60 s to reach tempera-

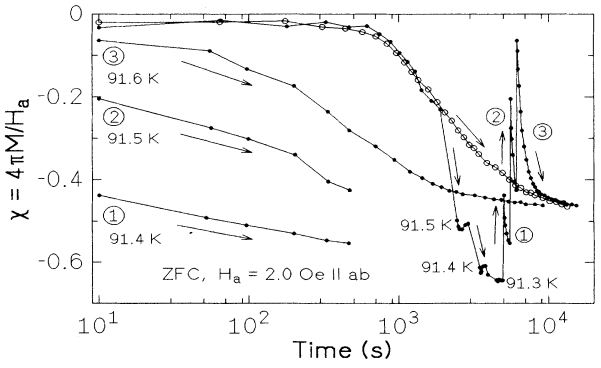

FIG. 2. Relaxation of ZFC susceptibility for single crystal B. An undisturbed (open circles) and a disturbed (solid circles) run containing three step decreases followed by reversed step increases in temperature. Details of temporal evolution of susceptibility after positive temperature changes (1–3) are seen by shifting to the left.

ture stability (±5 mK). An influence of temperature overshoots (< 50 mK) is assumed to be weak and short in time compared with the duration of each temperature change. Each step decrease in temperature ($\triangle T = -0.1$ K) results in a step increase in susceptibility followed by a slight decrease with time. This gives evidence of the existence of a "fast" and a "slow" response of the susceptibility to a step change in temperature.[17] The reversed temperature steps, in contrast, cause a stronger change of susceptibility followed by a much more pronounced time dependent increase. This behavior is in all details qualitatively comparable to nonmetallic spin glass findings, e.g., on $Cd_{0.6}Mn_{0.4}Te$, as reported by Lundgren and Nordblad.[17] The very nonsymmetric response on temperature changes $\triangle T$ is caused, we think, by a hierarchical organization (ultrametricity) of metastable states in phase space, as suggested in a number of theoretical papers[18,19] and applied to spin glasses[20,21] specifically for an explanation of the memory effect in $YBa_2Cu_3O_{7-\delta}$ single crystals.[22] It is assumed that metastable states (local energy minima) are separated by finite barriers with temperature dependent height. The barriers should increase steeply with decreasing temperature and diverge at lower temperatures.[20] This offers an explanation for our observation that the reported anomalous magnetic relaxation occurs only for temperatures above $\approx$ 88 K.

For common spin glasses the "slow" response is closely logarithmic in time.[23] In that context the time variation of the "slow" response of our crystals to the step increases in temperature can be investigated in more detail. For that purpose in Fig. 2 the time intervals of interest are shifted to the left to enlarge the time scale. After the first positive temperature step to $T = 91.4$ K the susceptibility displays a nearly perfect logarithmic time increase over the whole time interval ($\approx$400 s). The "slow" response upon the second positive temperature step to $T = 91.5$ K appears logarithmic in time up to $t \approx 150$ s and is then followed by a faster relaxation. For the "slow" response on the third step to $T = 91.6$ K there is merely an indication of a logarithmic time dependence for short times up to $t \approx 40$ s. For longer times the susceptibility asymptotically approaches the undisturbed run. The temporal range of the logarithmic part of the "slow" response decreases strongly with increasing temperature. This is an indication of ultrametricity. However, the temperature steps do not destroy the initial landscape of metastable states and therefore do not wash out the "memory" determined by the starting conditions.

Figure 3 shows a ZFC magnetic relaxation measurement for crystal B at $T = 91.6$ K and $H_a = 2$ Oe $\|ab$, and a repeated measurement with the same starting conditions. At $t = 1360$ s the temperature is raised up to 91.7 K and at $t = 1760$ s it is lowered back to 91.6 K. The "fast" response produces a smaller step decrease in susceptibility than in Fig. 2, but note that the starting susceptibility at the steps was lower. Zero susceptibility seems to be a natural limit and correspondingly the "slow" response exhibits a different time dependence as compared with Fig. 2. Paramagnetic moments do not occur. If spontaneous supercurrents, caused by π junctions inside the network of Josephson junctions, are responsible for the suppression of diamagnetism, an energy argument elucidates the limit. The condensation energy is the source for a creation of spontaneous magnetic flux by circulating supercurrents.[24] The energy needed to produce a paramagnetic susceptibility would exceed the provided condensation energy. We have used the term "spin glass" for brevity. Probably it comes closer to reality thinking of a glass of orbital moments, possibly formed by such Josephson loops.

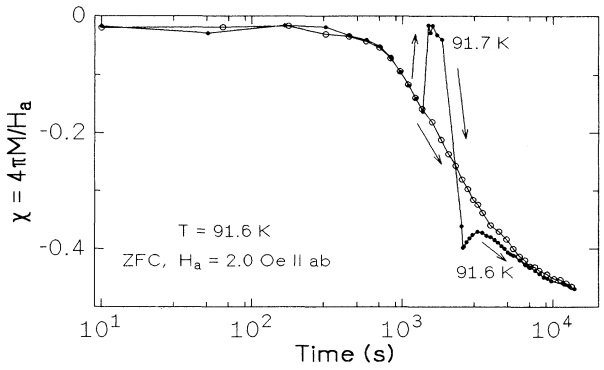

FIG. 3. The same as Fig. 2, but positive temperature step first, showing the $\chi = 0$ appears as a natural limit.

In summary, we have found an anomalous magnetic relaxation for $YBa_2Cu_3O_{7-\delta}$ single crystals. The diamagnetic magnetization *increases* nonlogarithmically with time. Shape and size of the effect are widely reminiscent of spin-glass-type relaxation. A "fast" and a "slow" response of magnetization upon step decreases or increases in temperature is found, quite similar particularly to *nonmetallic* spin glasses. The "slow" response for warming steps (Fig. 2) shows the same time dependence as reported for spin glasses by Lundgren *et al.*[23] Other than the droplet model[25] it is only the hierarchical picture of metastable states in phase space that is able to explain the very nonsymmetrical behavior of the "slow" response on cooling or warming steps, respectively. This asymmetry is responsible for the recently reported "quasihysteretic" behavior of magnetization with temperature.[8]

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