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Relaxation-caused suppression of magnetization in superconducting $YBa_2Cu_3O_{7-\delta}$ single crystals

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Stepwise zero-field-cooled, field-cooled-cooling (FCC), and field-cooled-warming (FCW) magnetization measurements have been made on $YBa_2Cu_3O_{7-\delta}$ single crystals in small magnetic fields applied in the *ab* plane and along the *c* axis. In a narrow temperature range below the FCC-T_c onset (≈ 2 K) the magnetization shows "quasihysteretic" behavior in temperature. FCC and FCW paths do not coincide, FCW having lower magnetizations. We interpret the accompanying lower FCW-T_c onset, in analogy to findings on nonmetallic spin glasses, as a result of the continuous succession of temperature steps.

Glasslike behavior of high-T_c superconductors was reported by Müller, Takashige, and Bednorz[1] who detected a "quasi de Almeida–Thouless" or irreversibility line when distinguishing between reversible and irreversible behavior of the magnetic susceptibility. Alternatively, Yeshurun and Malozemoff[2] explained such an irreversibility line by a more conventional "giant-flux-creep" model. Some magnetic properties of high-T_c superconductors, e.g., nonlogarithmic relaxation for polycrystalline $YBa_2Cu_3O_{7-\delta}$ (Ref. 3) or aging and memory effects for single-crystalline $YBa_2Cu_3O_{7-\delta}$,[4] support the superconducting glass model.[5] In contrast with known magnetization data on high-T_c superconductors we have found an irreversibility 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 field-cooled-cooling (FCC) and field-cooled-warming (FCW) magnetization. We will explain this in terms of a spin-glass theory which is based on a hierarchical organization of metastable states in phase space[6] that yields a nonsymmetrical response of magnetization on the sign of temperature changes ΔT.[7]

We present data for two double-twinned single crystals of $YBa_2Cu_3O_{7-\delta}$ with dimensions of $1.6\times1.1\times0.1$ mm^3 ($m=875$ μg) and $1.2\times1.2\times0.1$ mm^3 ($m=910$ μg). Both crystals, denoted as *A* and *B* have twin boundaries running along both the $\langle 110\rangle$ and $\langle 1\bar{1}0\rangle$ directions as seen under a polarizing optical microscope. No macroscopic single-twinned domains are detected. The method of crystal growth uses an off-stoichiometric composition rich in BaO and CuO. Samples are grown in yttria stabilized zirconia crucibles in air and post annealed in flowing oxygen. During annealing the furnace is kept at 450 °C for four days and cooled to room temperature in 24 h, all with flowing oxygen. For more details of crystal growth see Ref. 8. Inductively coupled plasma–Auger electron spectroscopy analysis yields magnetic impurity concentrations of Fe and Mn below 6 ppm and 0.2 ppm, respectively.

A commercial superconducting-quantum-interference-device (SQUID) magnetometer (Quantum Design, Inc.) was used for magnetization measurements. The sample holder consists of a small sheet of paper inside a soda straw which is mounted on the sample rod. The single crystals were glued onto the paper with UHU hart. Since the ends of the paper did not pass through the magnetometer coils while the data were taken, the paper made a negligible contribution to the signal. The signal of the soda straw and of the glue is also negligible, even at low fields where the diamagnetic signal originating from the samples is small. Paramagnetic influences caused by oxygen contamination using paper are also negligible. Temperature and field stabilities were carefully checked. To avoid overshoots the temperature was varied by 0.1-K or 0.2-K steps for $\sim$10-K spans about $T_c(H)$. Below and above this region the temperature was changed by 1 or 2 K per step. The magnetic-history-dependent remanent field of the used superconducting magnet is accounted for by comparison with high-quality Nb samples with nearly the same demagnetization factor and mass as our crystals.

The zero-field-cooled (ZFC) path is measured by cooling the sample in zero field ($H\leq0.05$ Oe) applying the field at low temperatures (normally 10 K), and then measuring the resulting magnetization with increasing temperature. The ZFC magnetization corresponds to the diamagnetic shielding effect. The field-cooled-cooling (FCC) magnetization, which represents the Meissner effect, is measured with *decreasing* temperature in a constant field, first applied at a temperature $T>T_c$ (normally 120 K). The field-cooled-warming (FCW) magnetization is measured after carrying an FCC process down to 10 K, as a function of *increasing* temperature in a constant field. A temperature step increase at $\Delta T=+0.1$ K (ZFC and FCW measurements) requires a time of approximately 270 s and a step decrease in temperature (FCC) about 570 s. The required time for larger steps, $|\Delta T|<0.5$ K, is independent of its width.

Both samples show very similar behavior in all features. We therefore restrict ourselves in displaying measurements for crystal *A* only. Figure 1(a) shows ZFC, FCC, and FCW magnetization curves for $H_a=1$ Oe $\|ab$. The demagnetization factor n is calculated from the slope of the Meissner region of the magnetization curve $M(H_a)$ to be $n_\|=0.05$ for $H_a\|ab$ and $n_\perp=0.86$ for $H_a\perp ab$. Corresponding values of n obtained from ellipsoidal approximations are in good agreement with those

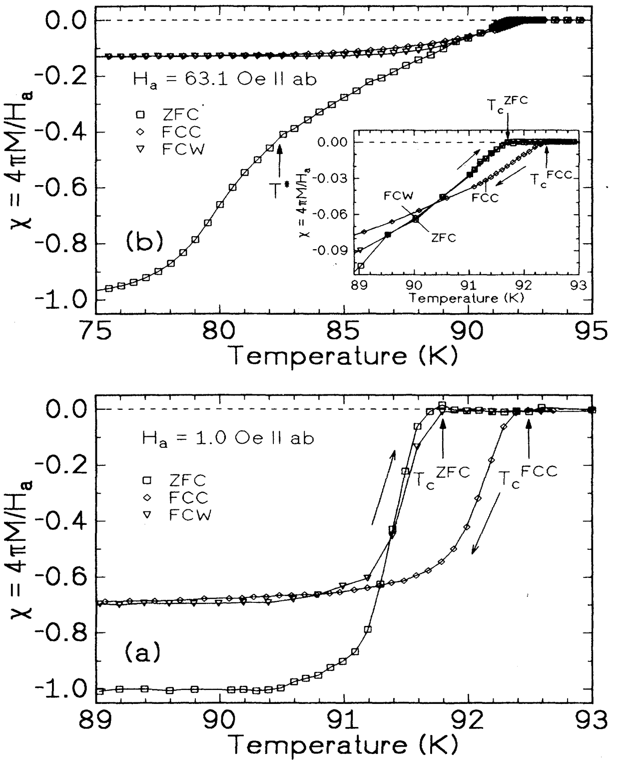

FIG. 1. ZFC, FCC, and FCW magnetizations for sample *A* with a 1-Oe (a) and a 63.1-Oe (b) applied field $H_a \| ab$ planes. The inset in (b) shows the quasihysteretic range on an enlarged scale. Different onset temperatures $T_c^{\rm ZFC}=T_c^{\rm FCW}$ and $T_c^{\rm FCC}$ are denoted by arrows.

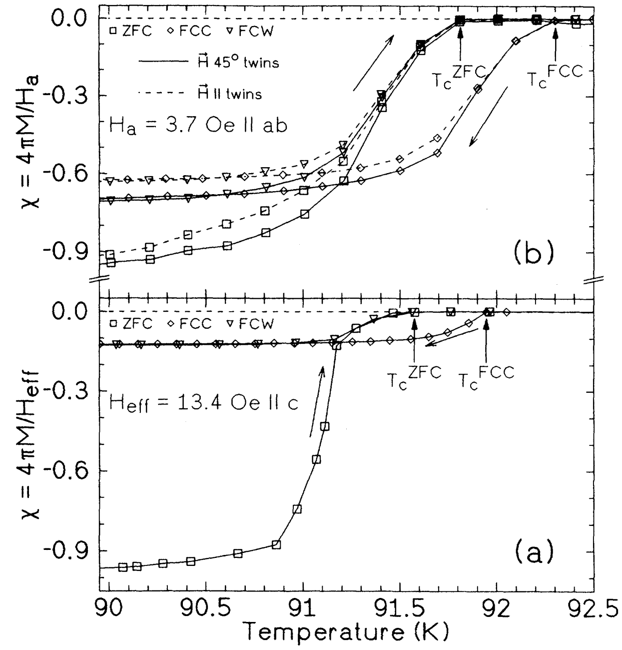

FIG. 2. Temperature dependence of the magnetization for different orientations of the field with respect to *ab* planes and twinning planes (TP's). (a) $H_a \perp ab$ planes, corrected for $n_\perp=0.86$. (b) $H_a \| ab$ planes, and H_a parallel (dashed lines) or 45° from TP's (full lines).

extracted from the slope. In Fig. 1(b), taken at $H_a=63.1$ Oe $\|ab$, a common feature with known magnetizations, namely the knee in the ZFC curve, is displayed at the temperature T^* at which the flux fronts meet the center.[9] The main difference between known $M(T)$ data and our measurements is the irreversibility of FCC and FCW data in a temperature range $\Delta T_h \approx 0.6$ K below the first occurrence of diamagnetism at $T=92.3$ K, Fig. 1(a). This "quasihysteretic" behavior in temperature produces lower magnetization values on warming and higher ones on cooling the sample. The very narrow magnetic transition width (10–90 %), about 0.5 K for the ZFC curve at $H_a=1$ Oe, underlines the high quality of the sample. We define different onset temperatures $T_c^{\rm ZFC}(H_a)$, $T_c^{\rm FCC}(H_a)$, and $T_c^{\rm FCW}$ as the intercept of a linear extrapolation of the magnetization in the diamagnetic state with the normal-state base line. Note that ZFC and FCW curves coincide for the smaller magnetization of the Meissner path upon warming (FCW). This may define an irreversibility temperature T_h to be derived from merging ZFC and FCW instead of ZFC and FCC. The remarkable difference between $T_c^{\rm ZFC}=T_c^{\rm FCW}=91.7$ K and $T_c^{\rm FCC}=92.3$ K, denoted above as ΔT_h, is nearly field independent [see Figs. 1(a) and (b)]. This difference is shown to be not affected by choosing identical times (600s) for temperature steps in both paths (FCC and FCW). Even when the temporal sequence of ZFC, FCC, and FCW measurements is changed, this neither affects the occurrence of different T_c's nor the temperature width of this quasihysteretic effect.

A very similar curious feature is reported by Datta *et al.*[10] These authors have found an irreversibility in the FCC and FCW data of oxygen-deficient polycrystalline $YBa_2Cu_3O_{7-\delta}$ but only in a region further below T_c, without having different onset temperatures. In a paper by Krusin-Elbaum *et al.*[11], Figs. 2 and 3 display an overlap of FC and ZFC curves. No comment has been made, except for the possibility of experimental uncertainty. Figure 1 in Ref. 12 displays similar overlapping, with no comment made by the authors either.

Figure 2(a) shows magnetization measurements at H_a *perpendicular* to the *ab* plane with demagnetization factor $n_\perp=0.86$. The values of T_c for ZFC and FCC are nearly the same as for the $H_a \| ab$ orientation. We conclude, therefore, that there is no anisotropy of this quasihysteresis. The small value of the Meissner fraction $\mathrm{MF}=-4\pi M_{\rm FC}/H_a$ $[\mathrm{MF}(H_{\rm eff}=13.4\ \mathrm{Oe})=0.13]$ for $H_a \perp ab$ is consistent with reported values.[13] It is easy to imagine that vortices parallel to twinning plane crossings are strongly pinned.[14]

Figure 2(b) shows ZFC, FCC, and FCW magnetization measurements on sample *A* at $H_a=3.7$ Oe for two different field orientations in the *ab* plane with respect to the intersecting twin planes. The first set (full lines) is obtained for an angle $\alpha=45°$ between H_a and TP's oriented in both the $\langle 110 \rangle$ and the $\langle 1\bar{1}0 \rangle$ directions. The angle for the second set (broken lines) was 0° and 90°, respectively (parallel mode). As is seen the occurrence of different onset temperatures is not influenced by different field orientations with respect to TP's. According to Liu *et al.*[15] the slightly lower MF=0.67 in the parallel mode provides evidence of stronger pinning than in the other orientation (MF=0.73). Concluding this section we state that there is no significant anisotropy for the different onset temperatures $T_c^{\rm ZFC}$, $T_c^{\rm FCC}$, and $T_c^{\rm FCW}$. No influence of magnetic field orientation related to twinning planes on this effect has been observed.

After the above measurements sample *A* has been broken into two pieces with masses $m_{A1}=370$ μg and $m_{A2}=310$ μg. For the 370-μg sample, denoted as *A*1, ZFC, FCC, and FCW magnetization runs at $H_a=3.7$ Oe $\|ab$ have been performed. Similar magnetization curves were obtained as for the former sample *A*. The different onset temperatures to diamagnetic response are $T_c^{\rm ZFC}=91.6$ K and $T_c^{\rm FCC}=92.1$ K for ZFC and FCC runs, respectively. The Meissner fraction is found to be MF=0.70. Comparison with Figs. 1(a) and (b) rules out that the observed magnetization anomaly depends on sample shape.

The 310-μg sample, denoted as *A*2, was again oxygen annealed as described above, in order to check whether possible oxygen deficiency would be responsible for the hysteretic effect. Measurements under exactly the same conditions, e.g., field strength, orientation, and temperature sweep rate, show no difference in the hysteretic behavior of magnetization, except for an increase of MF at $H_a^{\|}=1$ Oe from $\mathrm{MF}_A=0.70$ up to $\mathrm{MF}_{A2}=0.90$.

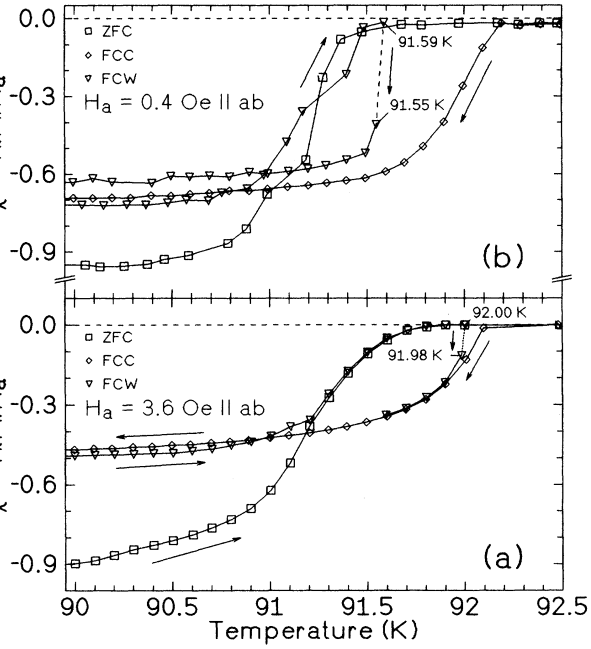

FIG. 3. Quasihysteretic temperature dependence of FCW magnetization with temperature reversals at 92.0 K (a) and 91.6 K (b) for magnetic fields $H_a\|ab$. The direction of temperature steps is denoted by arrows. The two dashed lines represent the first small steps (20 and 40 mK) following the two temperature reversals.

To further clarify the hysteretic behavior of magnetization in temperature we performed a set of measurements in which the direction of temperature changes in the range between $T_c^{\rm FCC}$ and $T_c^{\rm FCW}$ for the FCW runs was reversed. Figure 3(a) displays ZFC, FCC,and FCW data for $H_a=3.6$ Oe$\|ab$. After the FCW run was performed up to $T=92.0$ K, as described before, the temperature direction was reversed by a *small* temperature step $\Delta T=-20$ mK. This leads to a *strong increase* in magnetization. For the following steps of $\Delta T=-0.1$ K the magnetization reproduces the former FCC data perfectly. For the smaller applied field $H_a=0.4$ Oe$\|ab$ [Fig. 3(b)] the magnetization after the reversal at $T=91.6$ K differs somewhat from that of the FCC run. This is partly caused by stronger pinning of penetrated flux in comparison with the reversal at $T=92.0$ K [Fig. 3(a)], and by experimental resolution. The general response is as for 3.6 Oe.

The most remarkable feature is the dependence of magnetization on the direction of temperature change, as predicted by a hierarchical picture for spin glasses.[7] Our interpretation is based on the observation of a "fast" and a "slow" response to a step change in temperature made for spin glasses.[16] In contrast to metallic spin glasses, which show an overall decrease of magnetization with time, semiconducting or insulating spin glasses exhibit a nonsymmetrical response upon cooling or heating steps. For a semiconducting spin glass, e.g., $\mathrm{Cd_{0.6}Mn_{0.4}Te}$,[17] a step *decrease* in temperature yields a sudden increase (fast response) in FC susceptibility followed by a slight decrease with time (slow response). After a step *increase* in temperature the ZFC susceptibility decreases abruptly (fast) and increases with time (slow) much more than for the cooling step. Continuous successions of such steps in either direction yield the observed curve shapes FCC (for a number of step decreases) and FCW and ZFC (for a number of step increases) and therefore the different onset temperatures $T_c^{\rm FCC}$ and $T_c^{\rm FCW}=T_c^{\rm ZFC}$.

The question about the physical origin of the unusual quasihysteretic and spin-glass-type features of the magnetization now arises. Note that the properties of *semiconducting* spin glasses had to be used. Thus one is led to assume that we deal with a spin-glass coupling which is weak and short ranged.[18] Müller *et al.*[19] have reported on pronounced anomalies of the absorption and dispersion of the sound-induced rf magnetic field in polycrystalline $\mathrm{YBa_2Cu_3O_{7-\delta}}$ ($\delta<0.15$). These anomalies at 90 K and at 170 K are sensitive to thermal cycling and are interpreted as being due to ferroelectric phase transitions originating from oxygen jumps in Cu(1)-O(1) zigzag chains. This zigzag configuration is found by Mössbauer emission study[20] to be dynamic with a relaxation time $>10^{-7}$ s. Further, there is a similarity between ferroelectric phase transitions and peaks in elastic energy loss in $\mathrm{YBa_2Cu_3O_{7-\delta}}$ found by Cannelli *et al.*[21] These peaks are also dependent on thermal cycling and were observed only on heating or on cooling with a preceding aging below T_c and *not* on simply cooling. They are interpreted as being due to thermally activated processes such as oxygen jumping in zigzag Cu-O chains. A Josephson-coupled layer model[2] does not seem to be able to explain our experimental findings. A crossover from three- to two-dimensional superconductivity should produce anisotropic effects. For $H_a \perp ab$ planes, Josephson coupling should not affect the magnetization.[23] Also, it would be difficult to apply the concept of a vortex glass transition[24] to the quasihysteresis. Further, differing magnetization response upon flux expulsion or flux penetration due to the Bean-Livingston surface barrier[25] ought to be anisotropic and therefore excluded. Evidence for the influence of such surface barriers is only found for untwinned $YBa_2Cu_3O_{7-\delta}$ single crystals.[26]

In conclusion, our magnetization curves are to be interpreted as the result of a continuous sequence of step decreases (FCC) or increases (ZFC, FCW) in temperature. Each temperature step in the critical region causes a magnetic- *and* temperature-history-dependent response. We suppose a nonsymmetrical behavior of the fast response on cooling and warming steps, respectively. On warming, superconductivity is suppressed at lower temperatures than nucleation occurs on cooling. Several authors[4,17,27] have considered the spin-glass model and the flux-pinning model as limiting cases of the same physical picture. The features of our results support the view that for temperatures close to T_c glassy properties are dominating. Further studies, particularly direct relaxation measurements including temperature steps, are in progress.[28]

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