Observation of glass behavior at low fields in polycrystalline $YBa_2Cu_3O_7$

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We have measured the magnetic susceptibility of $YBa_2Cu_3O_7$ at low fields and observed a glass transition at $T_g < T_c$. This glass behavior, which is different from the vortex glass-fluid transition at high fields, can be interpreted as due to a Josephson weak-link effect. T_g shifts to lower temperatures with increasing applied field and is completely suppressed at higher fields, where $\chi(T)$ shows typical diamagnetic behavior. As $H \rightarrow 0$, T_g initially increases as the pressure on the sample pellet is increased and then saturates at higher pellet pressures. The pellet pressure dependence of H_d, the field necessary to suppress the glass state, is qualitatively consistent with theoretical prediction, that is, it is inversely proportional to the projected area normal to the field for an average loop of connected superconducting regions.

INTRODUCTION

Studies of the low-field magnetization of ceramic high-T_c cuprate superconductors have received renewed interest recently. Braunisch and co-workers[1,2] and Svedlindh *et al.*[3] have shown that for some Bi-based polycrsytalline superconductors, the dc field-cooled (FC) magnetization below the superconducting transition temperature T_c becomes paramagnetic at fields $H < 0.1$ Oe. This behavior is completely opposite to the normally observed "Meissner effect." Braunisch *et al.* explained their results in terms of orbital paramagnetic moments due to spontaneous currents which may originate in so-called π contacts in the weak-link network of crystallites in polycrystalline materials. Riedling *et al.*[4] also reported similar behavior, i.e., a positive FC magnetization, measured at larger fields, i.e., $H \leq 7$ Oe, for $YBa_2Cu_3O_7$ single crystals; in these measurements the sample was first cooled to low temperatures in a dc magnetic field, and data were taken as the sample was warmed up. In addition, for both Bi-based polycrystals and Y-based single crystals the temperature dependence of the FC magnetization at low fields[1,2,4] showed a diamagnetic dip just below T_c. It was observed[5] that the size of the diamagnetic dip just below T_c is strongly affected by the initial cooling procedure. In particular, the dip size is greatly enhanced by rapid cooling and essentially vanishes if the sample is cooled very slowly.

Theoretically, Kusmartsev proposed an orbital glass model[6] which is related to the existence of special loops of Josephson junctions with positive and negative Josephson couplings. With an odd number of negative couplings on the loop, a spontaneous orbital moment is created and accounts for the FC paramagnetic signal. Sigrist and Rice[7] explained the paramagnetic effect by a model of a Josephson network of d-wave superconductors. Dominguez, Jagla, and Balseiro[8] proposed a phenomenological theory which is also based on the existence of a network of Josephson junctions and supports the idea of an orbital glass description of the high-T_c compounds.

To further study the Josephson weak-link effect on low-field magnetization and at the same time avoid the complexity associated with cooling rates for a field-cooled procedure, we have measured the zero-field-cooled (ZFC) magnetic susceptibility of polycrystalline $YBa_2Cu_3O_7$. The results show that the temperature dependence of the ZFC magnetization at low fields exhibits a peak at a characteristic temperature T_g followed by a diamagnetic dip close to T_c, similar to that observed for the FC measurements.[1,2,4] The peak changes to a plateau as the applied field is increased. This plateau has also been observed in ac magnetization measurements.[9] We have determined the field and sample density dependence of T_g. This dependence will be discussed in terms of the size of Josephson loops in the ceramic high-T_c superconductors.

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EXPERIMENTAL

The polycrystalline $YBa_2Cu_3O_7$ samples studied here were prepared using the solid-state reaction technique. The appropriate amounts of high purity Y_2O_3, $BaCO_3$, and CuO were thoroughly mixed and then pressed into pellets $\frac{3}{4}$ in. in diameter and about $\frac{1}{8}$ in. thick using four different pressures, i.e., $P=1.87$, 2.18, 2.81, and 3.43 kbar for samples *S*-1, *S*-2, *S*-3, and *S*-4, respectively. The pellets were reacted in air at 950 °C for 16 h. They were then ground to a fine powder and the entire procedure was repeated. After the materials were sintered in air twice, they were again ground to a fine powder, mixed, pressed into pellets, and finally annealed in flowing oxygen for 16 h. Note that the pressure was kept the same for every individual sample as it was pressed to form a pellet. The lattice parameters which were measured by powder x-ray diffraction at room temperature are essentially the same for all samples and are consistent with those previously published.[10] We also investigated these samples using the backscattered electron image technique and energy-dispersive analysis of x rays by using a scanning electron microscope. We found no evidence of a second phase. The typical size of grains is about 10 μm for the samples pressed at higher pressures, i.e., 2.81 and 3.43 kbar, and is smaller for samples pressed at lower pressures, i.e., 2.18 and 1.87 kbar. The microvoid volume of the higher pressure samples is, however, smaller than that of the lower pressure samples. Scanning electron micrographs at different magnifications of the *S*-3 sample at $P=2.81$ kbar are shown in Figs. 1(a) and 1(b). It can be clearly seen from Fig. 1(b) that the microcrystals grew layer by layer along the *c* axis implying a very low surface energy within *a*-*b* planes, i.e., the (001) surface. A similar structure to this terracelike circular-layered microstructure observed by us has been reported previously in the case of single-crystal growth of $YBa_2Cu_3O_7$.[11] The magnetic susceptibility was measured using a commercial Quantum Design superconducting quantum interference device (SQUID) magnetometer. The samples used for magnetization measurements were cut into a square bar with dimensions of about $0.5\times0.5\times6$ mm^3. Samples were initially cooled in zero field from $T>T_c$ to 5 K. Then a field was applied, and the ZFC data were taken as a function of increasing temperature up to $T>T_c$. The FC data were then measured by decreasing the temperature to 5 K in the same field. Since these measurements were performed in low fields, certain necessary precautions were taken. In particular, a calibration of zero field (to within ±0.2 G) was obtained by using a high purity Pd sphere to determine the residual field in the magnetometer solenoid. In our magnetometer the sample was moved through the SQUID pickup coils with a scan length of 4 cm, so that the samples were exposed to magnetic-field variations of no more than 0.2%, making induced moments due to field variation inconsequential.

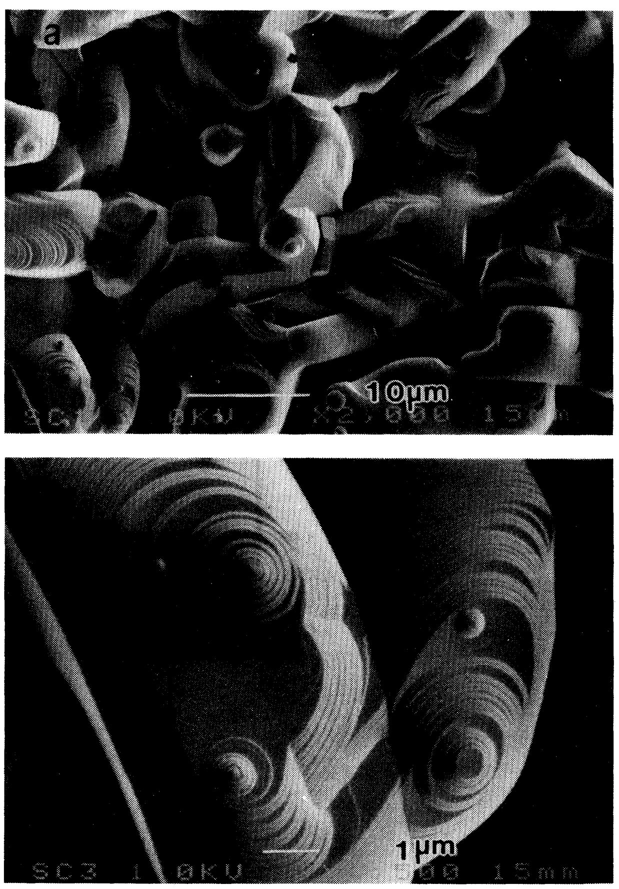

FIG. 1. Scanning electron micrographs of the *S*-3 $YBa_2Cu_3O_7$ sample pressed at $p=2.81$ kbar. (a) Magnification of 2000. (b) Two crystallites, at the lower left of (a), magnified 8500.

RESULTS AND DISCUSSION

Shown in Fig. 2 is the temperature dependence of the magnetic susceptibility χ measured at $H=5$ Oe for three

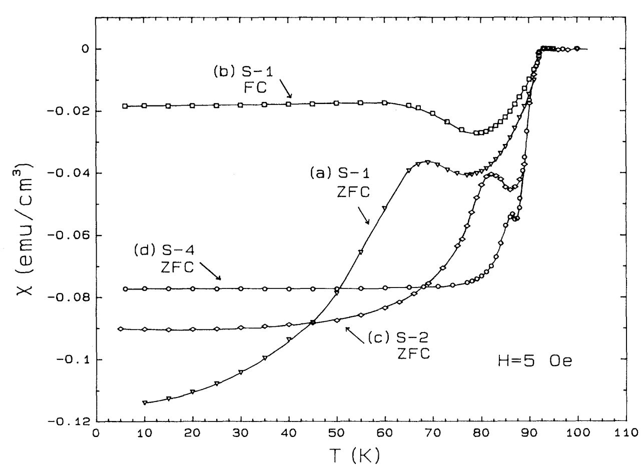

FIG. 2. $\chi(T)$ of $YBa_2Cu_3O_7$ measured at $H=5$ Oe for three samples with different pressures. (a) ZFC data for *S*-1 pressed at $p=1.87$ kbar, (b) FC data for *S*-1 (the sample was cooled very rapidly to 10 K in a field of 5 Oe and data were taken while warming the sample), (c) ZFC data for *S*-2 pressed at 2.18 kbar, and (d) ZFC data for *S*-4 pressed at 3.43 kbar.

samples with different pressures. The χ data were calculated by using the x-ray density and correcting for the demagnetization factor. The demagnetization factor introduces a 5% uncertainty. Curve (a) is the ZFC data for the S-1 sample pressed at $p=1.87$ kbar. Note that the absolute value of χ at 10 K is much greater than $1/4\pi$ because the microvoid volume of this sample is totally shielded in a field of 5 Oe. χ increases with increasing temperature and reaches a peak at $T_g=70$ K. Then it decreases, passes through a minimum and finally increases again up to T_c at 92 K. The S-1 sample was then cooled very rapidly at $H=5$ Oe from 150 to 5 K, and the FC data were taken while warming the sample. The FC data of the S-1 sample are shown as curve (b) in Fig. 2. The diamagnetic dip just below T_c in the FC curve is similar to dips reported recently,[5] and is influenced by the cooling rate in the FC procedure as mentioned earlier. However, the peak behavior in the ZFC curve is not influenced by the warming rate during the measurements. The ZFC data for S-2 with $P=2.18$ kbar and S-4 with $P=3.43$ kbar are shown as curves (c) and (d) in Fig. 2, respectively. Curves (c) and (d) in Fig. 2 also show a peak followed by a diamagnetic dip. Note that T_g increases from S-1 to S-2 to S-4, i.e., T_g increases with increasing pellet pressure. It will be shown later that T_g versus pellet pressure saturates at higher pressures. We have also performed magnetization measurements on samples with different shapes. The values of T_g are not affected by sample shape. It should also be mentioned that we have measured $\chi(T)$ for a sample which did not receive the final oxygen anneal and for a sample that had been exposed to air for years. A diamagnetic dip was not present for these poor quality samples. This suggests that the diamagnetic dip is not an impurity effect.

The behavior discussed above, namely a peak followed by a diamagnetic dip, implies a transition at $T_g<T_c$. To more clearly understand the magnetic response below and above T_g, we have performed thermal cycling measurements of χ. Figure 3 shows irreversible behavior below T_g and reversible behavior above T_g for the S-2 sample. The sample was first cooled to 5 K (point a) in zero field. Then a field of $H=5$ Oe was applied and held fixed for the remainder of the cycle. The sample was then taken through a heating-cooling-reheating trajectory, i.e., heated from point a (5 K) to point b (76 K) then cooled to point c (10 K) and finally reheated to 76 K to point b' which is near but slightly below point b. The heating-cooling cycle, i.e., a to b and b to c, is clearly far more irreversible than the cooling-reheating cycle, i.e., b to c and c to b'. The sample was then taken through another heating-cooling-reheating trajectory starting from b', i.e., heated from b' to d to e then cooled from e to d to f and finally reheated from f to d to e. Note that the b' to d to f to d portion of the trajectory is very similar in behavior to the a to b to c to b' trajectory just discussed in that the heating-cooling cycle b' to d to f is far more irreversible than the cooling-reheating cycle d to f to d. However, when one considers the heating-cooling-reheating trajectory that starts at d, i.e., d to e to d to e, it is entirely reversible. Note that point d is at the peak temperature T_g. Hence it appears that χ or M shows irreversible behavior below T_g and reversible behavior above T_g.

This reversible behavior above T_g and irreversible behavior below T_g is characteristic of a glass transition, like that observed for spin-glass systems. T_g is defined as the glass transition temperature. Note that the value $H=5$ Oe is smaller than the lower critical field H_{c1} (at 82 K) and hence this glass transition is completely different from the vortex-glass–fluid transition at high fields, i.e., $H_{c1}<H<H_{c2}$.[12–14] The latter transition is a bulk superconducting property. It was mentioned earlier that several theoretical groups have proposed the orbital glass model for high-T_c superconductors.[6–8] They begin with a special loop of Josephson weak-link junctions and derive the glass behavior at low fields. The critical current I_c of the Josephson loops decreases with increasing temperature. At higher temperatures, i.e., $T_g<T<T_c$, decoupling between the grains occurs since I_c vanishes, and thus χ vs T shows typical diamagnetic behavior.

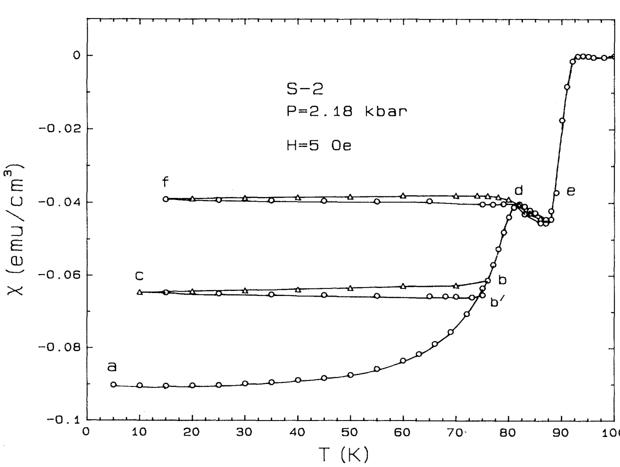

FIG. 3. $\chi(T)$ for the S-2 sample measured at $H=5$ Oe. Circles for heating and triangles for cooling.

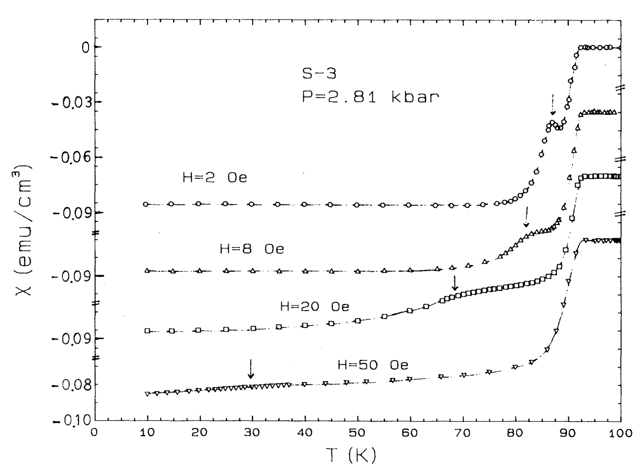

FIG. 4. $\chi(T)$ for the S-3 sample measured at $H=2$, 8, 20, and 50 Oe. Arrows show the glass transition temperatures.

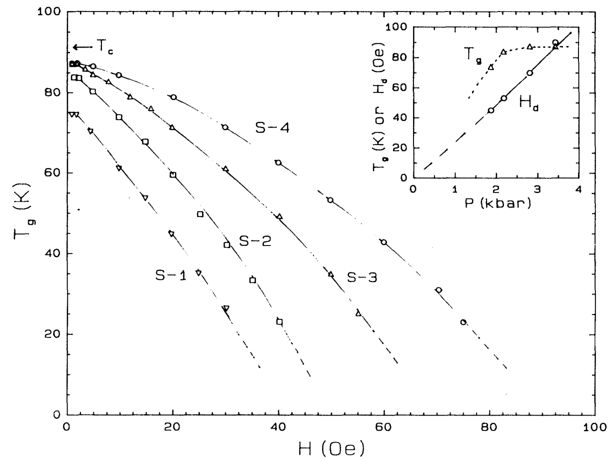

FIG. 5. T_g as a function of applied field for four samples with different pellet pressures. S-1 with 1.87 kbar, S-2 with 2.18 kbar, S-3 with 2.81 kbar, and S-4 with 3.43 kbar. Inset: T_g and H_d as a function of pellet pressure.

We have also measured the field dependence of the magnetic susceptibility for four samples. Shown in Fig. 4 are the χ data for sample S-3 (pellet pressure $P = 2.81$ kbar). At low fields a peak followed by a diamagnetic dip is observed (see $H = 2$ Oe curve). For higher fields the peak shifts to lower temperatures and evolves to a plateau. T_g is then best located from $d\chi/dT$, i.e., T_g is the temperature where $d\chi/dT$ is minimum. For fields higher than above 75 Oe it is essentially impossible to locate T_g and the χ curve exhibits a simple diamagnetic superconducting behavior. Since I_c is suppressed by the application of a magnetic field, one expects T_g to decrease with increasing applied field.

The field dependence of T_g for samples made at four different pellet pressures is shown in Fig. 5. We can see that for every sample T_g decreases monotonically with increasing applied field. Next consider how the values of T_g for H near zero depend on the pellet pressure. This is shown in the inset of Fig. 5. Note that T_g ($H = 0$) increases from 74 K for $p = 1.87$ kbar to 84 K for $p = 2.18$ kbar to 87.5 K for $p = 2.81$ kbar but then is unchanged for $p = 3.43$ kbar.

It has been proposed that the field H_d necessary for the coupling-decoupling transition is proportional to Φ/S,[15] where Φ is the flux quantum and S is the projected area normal to the field of an average loop of connected superconducting regions. If one extrapolates the highest pellet pressure sample curve, i.e., the S-4 curve of Fig. 5, to $T_g = 0$ to obtain the field H_d necessary to suppress the glass transition to $T = 0$, one obtains an H_d of about 90 Oe. H_d versus pellet pressure is shown in the inset of Fig. 5. Using $H_d \approx \Phi/S$ gives an S of about 3×10^{-9} cm^2 or a length scale $d \approx 5\times10^{-5}$ cm which is about 1/20th of the average crystallite size for the S-4 sample. As mentioned earlier the crystallite size is considerably smaller for the pellets fabricated at lower pressures but the volume fraction occupied by voids is considerably larger. In fact the average cross-sectional area of a void is higher for samples made at the lower pellet pressures. Hence it is quite possible that the projected area normal to the field for an average loop of connected superconducting regions is, in fact, larger for the lower pellet pressure samples even though the crystallite size is small. The inset of Fig. 5 shows H_d increasing linearly with pellet pressure. Hence the model $H_d \approx \Phi/S \approx p$ predicts that S should be inversely proportional to p. Future electron micrograph studies may allow us to determine the average normal cross-sectional area of voids and hence provide a check of the $S \approx 1/p$ relation.

In summary, zero-field-cooled magnetization studies presented here show that a glasslike transition occurs in polycrystalline high-T_c superconductors. The sensitivity of the transition to rather low magnetic fields and the relationship between H_d the field necessary to destroy the transition and void size both suggest that the transition is due to a Josephson weak-link effect.

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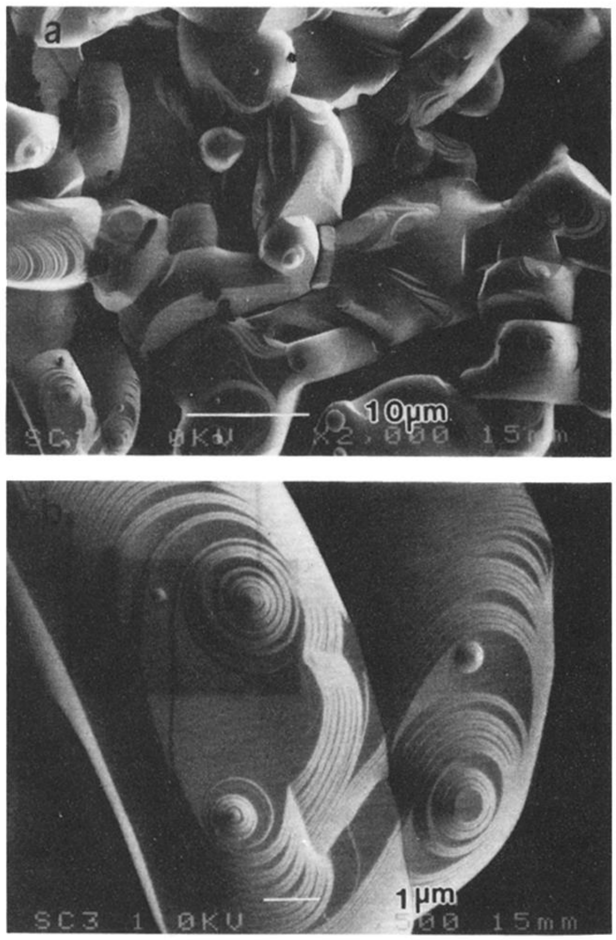

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