Bulk phase transition in $YBa_2Cu_3O_{7-\delta}$ single crystals

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Precise magnetization measurements of $YBa_2Cu_3O_{7-\delta}$ single crystals have found evidence for a bulk phase transition a few degrees below the superconducting critical temperature. The phase transition is indicated by a sudden drop of the lower critical field, $H_{c1}(T)$, separating a full coherent state at low fields and temperatures, the Meissner state, from a region at higher temperatures where magnetic excitations are induced at $H=0$.

Despite the great effort devoted to investigate the properties of high-temperature superconductors, their H-T phase diagram is far from being well established. In this Brief Report we present low-field magnetization measurements of $YBa_2Cu_3O_{7-\delta}$ single crystals showing a new phase transition indicated by an abrupt collapse of the lower critical field, $H_{c1}(T)$, a few degrees below the temperature, T_c, where bulk superconductivity appears.

The research was motivated by previous work,[1,2] showing that the reversibility line $T_R(H)$ and the melting line $T_M(H)$ are two different and well separated lines in the low-field region, which merge to a single one at higher fields.

In the context of the present paper, we call the reversibility line[3] the boundary in the H-T phase diagram, separating the high-field and temperature reversible dc magnetization region from the irreversible one found at lower fields and temperatures. The melting line is defined by the locus of the dissipation peaks measured[4] in mechanical oscillator experiments. The dissipation peak coincides with a fairly sharp change in the oscillator frequency. This phase boundary $T_M(H)$ separates a high field and temperature region where the coupling between the flux lines and the oscillating sample is null or very weak, from a lower field and temperature region where the vortices are strongly coupled to the sample.

Before the low-field data were available,[2] the controversy over $T_R(H)$ and $T_M(H)$ centered on whether they were a single physical phenomenon or separate features. The melting interpretation given in Ref. 4 points toward a softening of the elastic constants of the vortex lattice, while the reversibility line was interpreted[5] within a more standard picture of superconductivity with vortex depinning due to a thermally activated process.

The low-field data[1,2] have shown that $T_M(H)$ lies well below $T_R(H)$ and, what is more important, the sudden change in the elastic properties of the vortex lattice at $T_M(H)$ is not detected by the smooth and continuous variation of the temperature-dependent zero-field-cooled (ZFC) magnetization. This is important, since the ZFC magnetization for $T<T_R(H)$ is proportional to the critical current of the vortex state. These results indicate that the changes of the elastic characteristics of the magnetic flux structure take place without modifying the average number of vortices in the sample.

These findings, together with predictions of several theoretical models,[6,7] indicate that the low-field region of the phase diagram of the high-temperature superconductors should show interesting features related to the structure of the ensemble of vortices in these materials and support the idea that there is a lower temperature phase transition followed by a higher temperature depinning transition.

We have recently reported[8] that the lower critical field, $H_{c1}(T)$, of $YBa_2Cu_3O_{7-\delta}$ single crystals is quenched in a narrow range of temperatures, a few degrees below T_c.

In this Brief Report we provide experimental evidence proving that the collapse of $H_{c1}(T)$ at T_D is a bulk property induced by a phase transition, separating a superconducting coherent Meissner state throughout the sample from a noncoherent one at higher temperatures.

The magnetic flux measurements were done using a custom-built SQUID cryostat. In the 4–100 K temperature range the background magnetic signal was below 3 flux quanta per Oersted. The ambient field was reduced below 10 mOe by mumetal and superconducting magnetic shielding. The samples were mounted on top of a sapphire rod thermally connected to a liquid ^{4}He pot. The temperature of the sample was swept using an electrical heater mounted so as to avoid heat flow through the sample and thermometers. The thermal sweep rate was never faster than 2 K/min.

Four different single crystals from Bell Laboratories (that we identify as sample Nos. 1, 2, 3, and 4) have been measured, typically of 2 mm size in the a and b crystallographic directions and 40 μm in the c direction. No demagnetization corrections were taken into account when the applied field was parallel to the Cu-O planes (a-b planes). The demagnetization factor in the perpendicular direction was estimated to be about 0.95.

One single crystal from Argonne National Laboratories identified as sample No. 5 was also measured.

This crystal had a dimension of 1 mm in a-b crystallographic direction and 200 μm in the c direction, and is reported[9] to have twin boundaries in only 5% of its volume.

Figure 1 shows the ZFC and FC flux fraction [defined as the flux through the sample minus the flux through the sample at 10 K, $\Delta\Phi=\Delta\Phi(T)-\Phi(10\text{ K})$, normalized by the total flux expulsion, $\Delta\Phi_T=\Delta\Phi(T_c)-\Phi(10\text{ K})$] as a function of temperature for the No. 3 single crystal. The applied field was parallel to the Cu-O sheets, $H_{\parallel}=0.7$ Oe. The reversibility of the flux expulsion and the well defined temperature where it is first detected are indicative of the good quality of the single crystal. Complete reversibility of the FC and ZFC data is observed only at very low fields.

The ZFC flux fraction of the No. 5 sample is also shown for $H_{\parallel}=2$ Oe. The FC fraction at this field is 20% of the ZFC expulsion, lower than the 70% observed in the No. 1–No. 4 crystals, for equivalent fields. This result indicates that this single crystal, although less twinned, has a larger critical current. The inset in Fig. 1 shows the ZFC flux fraction of the No. 3 sample for different fields applied parallel to the a-b planes. The results shown in the figure are quite similar to those obtained for the other crystals. The scaling of the flux expulsion with field below a temperature T_{c1} is made evident in the same inset. The temperature dependence of the ZFC flux expulsion is characterized by a reversible temperature dependence below T_{c1} and an irreversible flux expulsion above it. The temperature T_{c1} is experimentally found by detecting the flux irreversibility by careful temperature cycling. In this way T_{c1} was determined to within 0.5 K. The arrows in the figure indicate T_{c1} for the different fields. This procedure was followed for the five crystals investigated. All samples showed a reversible temperature region below T_{c1} with a precision of three flux quanta.

The experimental ZFC flux expulsion below T_{c1} is reversible with temperature and directly proportional to the applied field. These are the two necessary conditions for the definition of the Meissner state. The $H_{c1}(T)$ is defined by the temperature T_{c1}.

The irreversible flux penetration has the same temperature characteristic in all the samples investigated. At T_{c1} the flux penetrates with an upturn curvature followed by an almost linear temperature dependence. The results of $H_{c1}(T)$ for the samples investigated are plotted in Fig. 2. Figure 2(a) shows the results for the samples Nos. 1 and 3 with the applied field parallel to the Cu-O planes, $H_{\parallel c1}$ (the results for the other sample measured in the same field direction were omitted for clarity). In the same figure we also have plotted the data for the perpendicular direction, $H_{\perp c1}$ (samples Nos. 1 and 4). Figure 2(b) shows $H_{\parallel c1}$ for the No. 5 crystal.

The most remarkable feature shown by the curves of Fig. 2 is the sudden drop of the $H_{c1}(T)$ below T_c. This drop is also detected in the curves of the inset of Fig. 1, where T_{c1} is seen to remain almost constant at a temperature T_D in the low-field curves. The $H_{\parallel c1}$ temperature dependence below T_D is linear in field up to the highest field measured of $H_{\parallel}=120$ Oe, with an extrapolation to $H=0$ that coincides with T_C (the onset critical temperature) for the No. 1–No. 4 samples and exceeds that tem-

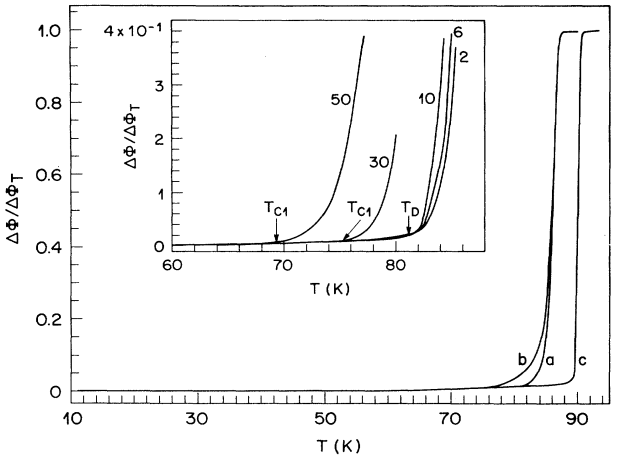

FIG. 1. ZFC (curve a) and FC (curve b) flux fraction (see text) as a function of temperature for the sample No. 3 with an applied field of $H_{\parallel}=0.7$ Oe and the ZFC (curve c) flux fraction for the sample No. 5 for an applied field of $H_{\parallel}=2$ Oe. The inset shows the ZFC flux fraction as a function of temperature for different applied fields for the sample No. 3. The numbers indicate the value of the applied field in Oersted.

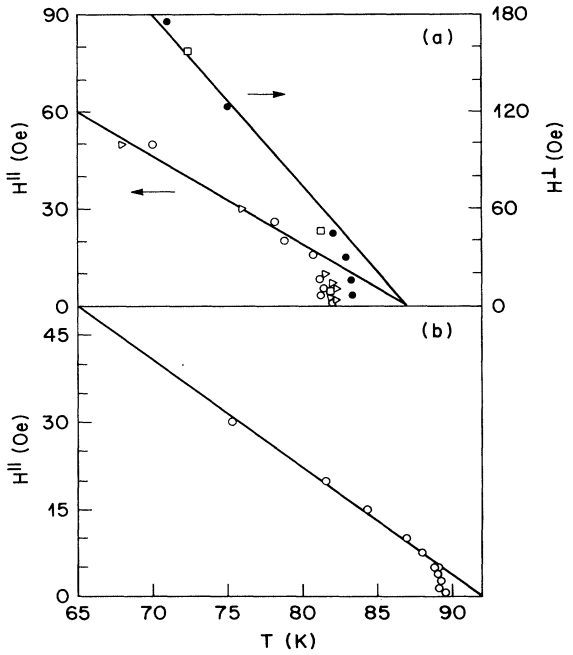

FIG. 2. Lower critical field, defined where irreversible flux penetration is observed, as a function of temperature. (a) Closed circles: $H_{\perp c1}$ for the sample No. 1; open squares: $H_{\perp c1}$ for the sample No. 4; open triangles: $H_{\parallel c1}$ for the sample No. 3; open circles: $H_{\parallel c1}$ for the sample No. 1. (b) Open circles: $H_{\parallel c1}$ for the sample No. 5. The solid lines are linear extrapolations of the high-field values.

perature by 1.5 K for the No. 5 sample.

In principle it is possible to think that our definition of $T_{c1}(H)$ could be associated to some particular region of the sample with a lower $H_{c1}(T)$, either due to the presence of sample inhomogeneities or local geometrical effects (corners, edges, etc.). Arguing against this possibility are qualitative and quantitative arguments and experimental evidence showing that $H_{c1}(T)$ is a bulk property. The parallel and perpendicular $H_{c1}(T)$, in the linear region, are in good agreement with those of Ref. 10, where a more elaborate criterion was used to define T_{c1}. It is difficult to believe that inhomogeneities or local properties of a given sample can be reproduced from sample to sample and it seems impossible that local properties can reproduce the anisotropy between $H_{\|c1}$ and $H_{\perp c1}$ in different single crystals. Also, if the $H_{c1}(T)$ is determined by a local demagnetization factor, the whole curve should be modified by a constant factor *without* changing its functional temperature dependence or the onset temperature. Other arguments suggesting that the drop of $H_{c1}(T)$ is due to a broad superconducting transition at $H=0$ can also be discarded. A broad temperature transition width should imply a broad distribution of lower critical fields. In this case, our definition of T_{c1} corresponds to the detection of the lowest $H_{c1}(T)$. The quenching of $H_{c1}(T)$ would imply that the lowest critical temperature (hypothetically associated to T_D) should have a corresponding $H_{c1}(T)$ with the steepest slope. This is inconsistent because the slope of $H_{c1}(T)$ at T_D implies a penetration depth $\lambda(0) \leq 300$ Å, which disagrees with the measured value.

We have provided qualitative arguments showing that $H_{c1}(T)$ is related to bulk properties. Now we will show through experimental data that the single crystals only have one critical temperature T_c, identified by the onset of the superconducting transition as measured by the SQUID (see Fig. 1). The corresponding transition width is much smaller than $T_C - T_D$. Figure 3 shows the temperature dependence of a zero-field remanent moment ZFRM, induced in the following way: The sample is cooled in zero field below T_D, the field is raised at a constant temperature to a value smaller than $H_{c1}(T)$. Then the temperature is raised until irreversible flux penetrates into the sample [care is taken to keep the temperature below the $T_{c1}(H)$ corresponding to the linear extrapolation of $H_{c1}(T)$; see Fig. 2], and, after that, the sample is cooled leaving flux locked into it, as shown in Fig. 3. The final step is to measure the temperature dependence of the remanent moment, induced after the applied field is reduced to zero. This procedure is repeated for different amounts of flux locked into the sample. All of the remanent moments were seen to disappear at T_c, to within 0.5 K. The results of Fig. 3 correspond to a trapped flux of only 0.5% of the total expulsion for this field. Results for other crystals were similar to those of Fig. 3, showing that the first penetration of irreversible flux takes place into a material that has a single T_c, well above T_D.

The investigation of the zero-field remanent moments turns out to be an important tool to show that the quenching of $H_{c1}(T)$ corresponds to a phase transition. To show this, the remanent moment was induced in a slightly different way. The sample is zero-field cooled and then the inducing field, H_i, is applied and reduced to zero at a constant temperature. The flux locked into the sample, if any, is determined by raising the temperature up to T_C and measuring the flux change. The flux locked into the sample as a function of H_i is shown in Fig. 4, for the No. 5 crystal. The results show that at 89.7 K flux is locked from $H_i=0$ while at $T=89$ K flux can only be locked once the $H_{c1}(T)$ has been reached [see Fig. 2(b)]. As a matter of fact, this is another way to measure $H_{c1}(T)$, giving the same results as those reported in Fig. 2. What is more important is that the amount of locked flux and its dependence on H_i is nearly the same for both curves if the curve of 89 K is shifted by 4 Oe. This shows that there is a very sharp line in the H-T phase diagram separating the two temperature regions in the low-field regime. Below T_D and for $H < H_{c1}(T)$ the sample

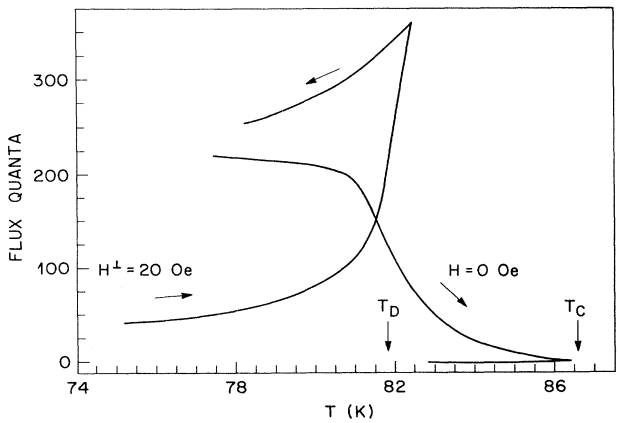

FIG. 3. Irreversible flux penetration and temperature dependence of the trapped flux after switching off the field (see text). The arrows indicate the thermal sweeps.

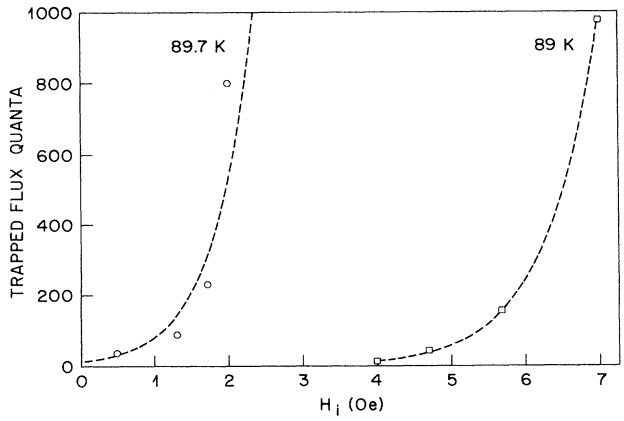

FIG. 4. Amount of trapped flux in the sample as a function of the inducing field H_i (see text) for the sample No. 5 at two different temperatures: (open circles) 89.7 K and (open squares) 89 K. The dashed lines are a guide for the eyes.

responds to a full coherent state, the Meissner state. Above T_D, $H_{c1}(T)$ drops to zero within the experimental resolution of a few flux quanta. This indicates that no permanent currents can flow around the surface to keep the sample free of magnetic excitations. From this point of view the transition resembles the two-dimensional Thouless-Kosterlitz transition.[11]

The strong temperature dependence of this phase transition and the experimental finding showing that it is present in the two crystallographic directions indicate that the transition is not induced by the magnetic field but rather by thermal energy. We would naturally expect that the temperature dependence of $H_{c1}(T)$ near T_D should show anisotropic behavior. With the present experimental resolution of our apparatus we cannot measure the transition line with enough precision to provide evidence of the expected anisotropy. It should be noted that all crystals have the same qualitative behavior of $H_{c1}(T)$. However, the temperature T_D differs from the linear extrapolation by 5 K for the No. 1–No. 4 crystals, while by only 2.5 K for No. 5.

It is difficult to speculate about the microscopic origin of the transition. Several authors[6] have proposed that the bulk character of the superconductivity is due to Josephson-like coupling between stacks of Cu-O layers. The transition reported here has the characteristics of a phase decoupling between superconducting regions. Whether these regions are the Cu-O stacks should be the subject of further research.

It is interesting to point out the qualitative resemblance between the experimental phase diagram reported here and that theoretically sketched in Fig. 2 of the paper by Fisher *et al.* (see Ref. 6). However, it is also important to mention some qualitative differences. It has been experimentally proven that the melting and reversibility lines are different. In particular, the reversibility line in the crystals investigated here is seen[12] to extrapolate to T_C and not to T_D. On the other hand, the dynamics of the flux motion is seen to change at T_D. These and many other questions related to the magnetic flux characteristics in the region $T_D < T < T_C$ remain open.

In conclusion, very precise measurements of the temperature and field limits where phase coherence can be established throughout the sample have allowed us to determine an additional transition line in the phase diagram of the $YBa_2Cu_3O_{7-\delta}$ system.

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