Thermodynamic Evidence for a Flux Line Lattice Melting Transition in $YBa_2Cu_3O_{7-\delta}$

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Moving- and stationary-sample SQUID magnetometry indicates discontinuous jumps of the magnetization of an untwinned single crystal of $YBa_2Cu_3O_{7-\delta}$. The location of these jumps in the H-T plane coincides with the location of the resistive drops measured on the same sample. These results demonstrate the existence of a first-order melting transition of the flux line lattice in $YBa_2Cu_3O_{7-\delta}$. [S0031-9007(96)00456-5]

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The phase diagram of the high temperature superconductors contains a vortex liquid phase which occupies a large part of the H-T plane below the mean field upper critical field, H_{c2}. Upon cooling, the flux line system transforms from the liquid into a solid state exhibiting zero linear resistance and the onset of a finite static shear modulus. The nature of this transformation has been the subject of extensive recent research. For a clean sample the transition into the flux line lattice phase is predicted to be of first order [1,2]. Recent Monte Carlo simulations for a three dimensional flux line system [3,4] support this behavior. In the presence of disorder due to point or correlated pinning the transition is believed to be continuous transition, possibly to a vortex glass [5–7] or a Bose glass [8]. In addition, due to the large anisotropies a decoupling transition [9,10] of vortex lines into vortex pancakes is expected.

In the case of clean, untwinned $YBa_2Cu_3O_{7-\delta}$ sharp drops of the resistivity in high magnetic fields [11–17] which are accompanied by the onset of non-Ohmic behavior as well as by hysteresis in their temperature and field dependence [11,14,16] are interpreted as manifestations of a first-order melting-freezing transition of the flux line system. Recent dc-transformer experiments [18] on untwinned $YBa_2Cu_3O_{7-\delta}$ indicate that these sharp drops coincide with the loss of **c**-axis coherence. However, transport measurements do not probe the defining characteristics of a magnetic first-order transition, that is, a discontinuity in the entropy (latent heat) accompanied by a discontinuity in the magnetization. Neutron scattering [19] and muon spin rotation [20] experiments on $Bi_2Sr_2CaCu_2O_8$ reveal abrupt changes in the line shapes consistent with the occurrence of a melting transition. SQUID measurements [21] and, in particular, magnetization measurements on single crystals of $Bi_2Sr_2CaCu_2O_8$ utilizing micro Hall probes [22] have shown very sharp jumps in the magnetization giving further support to the existence of a first-order vortex lattice melting transition. Previous measurements of the temperature dependence of the magnetization of $YBa_2Cu_3O_{7-\delta}$ indicate a jump in the magnetization [23]. Here, we present transport measurements and measurements of the field and temperature dependence of the magnetization of an untwinned crystal of $YBa_2Cu_3O_{7-\delta}$. Moving- and stationary-sample SQUID magnetometry indicates discontinuous jumps of the magnetization. The location of these jumps in the H-T plane coincides with the location of the resistive drops. These results demonstrate the existence of a first-order melting transition of the flux line lattice in $YBa_2Cu_3O_{7-\delta}$.

The sample used in this study is an untwinned single crystal of $YBa_2Cu_3O_{7-\delta}$ with a mass of 1.286 mg and approximate dimensions of $1.1 \times 0.7 \times 0.22$ mm^3. It has a transition temperature $T_c = 92.9$ K with a (magnetic) width of 0.3 K. The magnetization measurements reported here were performed in a Quantum Design SQUID magnetometer equipped with a 7 T high homogeneity magnet. The transport measurements were performed using standard lock-in techniques with a measuring current density of 0.65 A/cm^2 at a frequency of 23 Hz.

Inset (a) of Fig. 1 shows the magnetization at 84 K in increasing and decreasing fields applied parallel to the **c** axis. For these measurements the sample was cooled in

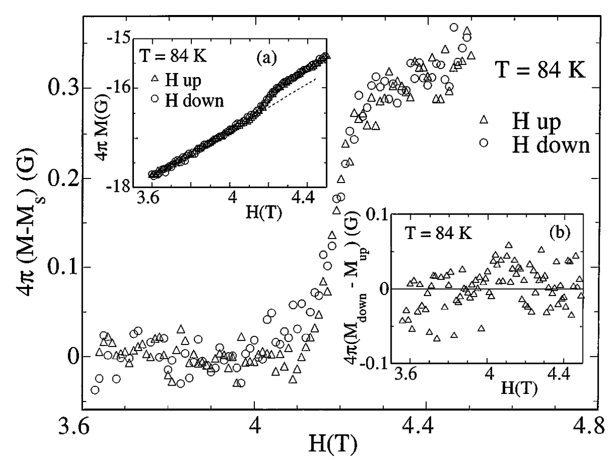

FIG. 1. Jump in the magnetization at 84 K measured in increasing and decreasing fields. Inset (a) shows the raw data. The dotted line represents a linear extrapolation of the low field variation. Inset (b) shows the magnetization hysteresis, $4\pi(M_{\text{down}} - M_{\text{up}})$.

the starting field of 3.6 T. After an equilibration time of 1 h data were taken in 100 G steps with a pause of 30 sec after each field step. The data display a marked jump of the magnetization at 4.2 T. This is clearly seen in the main panel of Fig. 1, where the magnetization is plotted relative to a linear extrapolation of the low field behavior, $4\pi M_s$, indicated by the dotted line in inset (a) of Fig. 1. The jump height, $4\pi \Delta M = 4\pi(M_l - M_s)$, is about 0.3 G occurring over a width of about 700 G. Here, M_l and M_s denote the magnetization in the liquid and solid states, respectively. It is important to note that the magnetization is reversible within the scatter of the data of about 0.05 G. This is shown in inset (b) of Fig. 1, displaying the magnetization hysteresis $4\pi(M_{\mathrm{down}} - M_{\mathrm{up}})$. Any residual irreversibility is smaller than the size of the magnetization jump by an order of magnitude, suggesting that the jump is not caused by some kind of depinning effect. A minimal detectable hysteresis of 0.05 G would correspond (using Bean's model for the present sample geometry) to a critical current density of 1.5 $\mathrm{A/cm^2}$. Thus, the apparent observation of zero resistance (see the inset of Fig. 3) is consistent with magnetic reversibility at our level of sensitivity. We note that the determination of a critical current density from transport measurements depends on the voltage criterion used in the nonlinear I-V curves. Within the resolution of the magnetization measurements the transition in increasing and decreasing fields occurs at the same field value even though the field dependence of the resistivity shows hysteresis of about 30 G. The jump height decreases rapidly with increasing temperature and drops below our resolution of 0.05 G at temperatures around 90.5 K (Fig. 2) which is well below T_c. This point will be discussed below.

A magnetization jump is also visible in the temperature dependence of the magnetization as shown in Fig. 3 for a field of 4.2 T. Around T_c the familiar broadening expected for superconducting fluctuations is seen [24]. Near 83.8 K a marked change in slope and a small discontinuity with a width of about 0.15 K occur. This is clearly seen when the data are plotted relative to a linear extrapolation of the low temperature behavior, $4\pi M_s$, as shown in the inset for several applied fields. The shift in the position of the jump and the reduction of the height are seen in correspondence to the $M(H)$ data shown in Fig. 2. Also shown is the temperature dependence of the resistivity in various fields applied parallel to the **c** axis. The resistive transitions show the familiar broadening at high temperatures followed by a sharp drop to zero resistance at the freezing temperature T_m. These data are typical for the behavior of clean samples as reported earlier. These results show that at temperatures corresponding to the drop to zero resistance a discontinuity in the magnetization occurs as expected for a first-order magnetic transition. The magnetic transitions display hardly any precursor effects due to critical fluctuations which are expected on both sides of a second-order transition. The positive value of $\Delta M = M_l - M_s$ implies that the vortex density in the liquid is higher than in the solid phase analogous to the behavior observed in $Bi_2Sr_2CaCu_2O_8$ [22]. The relative reduction in average vortex spacing, $\Delta a_0/a_0$, across the transition is $(2.5-5) \times 10^{-6}$ for the fields measured here. At 4.2 T this corresponds to an addition of about 10^4 vortices to the sample. The expansion on freezing is rather unusual for conventional atomic solids with the notable exceptions of water, Ce, and Ge. It has been suggested [25] that the entropy gain in a denser liquid of flexible entangled vortices with long-range interactions outweights the cost in potential energy of the additional vortices.

Figures 1 and 3 shown that the slopes $\partial M/\partial H$ and $\partial M/\partial T$ change across the transition. Thermodynamic

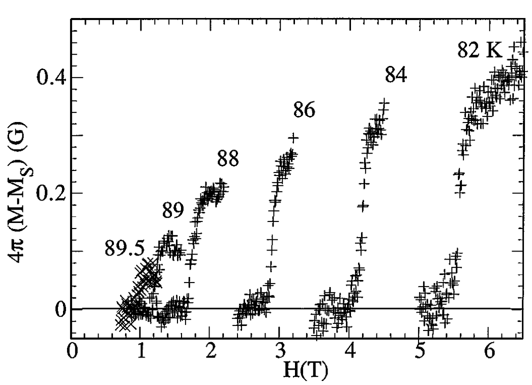

FIG. 2. Field dependence of the jump in the magnetization, $4\pi(M - M_s)$, at various temperatures.

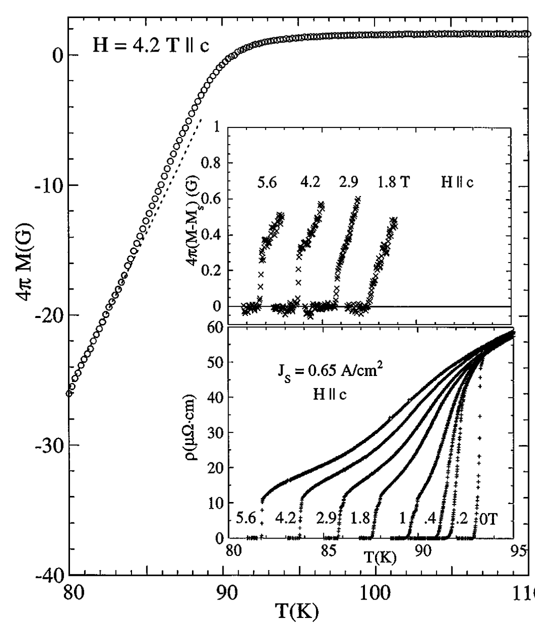

FIG. 3. Temperature dependence of the magnetization in 4.2 T. The dotted line represents a linear extrapolation of the low temperature variation. The inset shows the jump in the magnetization in several fields (top) and the temperature dependence of the resistivity in the indicated fields (bottom).

consistency requires that these slopes be related by $d(\Delta M)/dT = (\partial M_l/\partial T - \partial M_s/\partial T) + (\partial M_l/\partial H - \partial M_s/\partial H)dH_m/dT$. The partial derivatives are taken just below or about the transition. $H_m(T)$ is the phase boundary for the melting transition (melting line) as shown in Fig. 5. At 84 K the data in Figs. 1 and 3 indicate a value of 0.17 $\pm$ 40% G/K for $\partial M_l/\partial T - \partial M_s/\partial T$ as calculated with the above expression, whereas the experimental value is 0.2 $\pm$ 25% G/K. Even though the error bars are large (reflecting the uncertainties in determining the differences in slopes), the temperatures and field dependent data appear to be consistent.

It has been noted that the motion of the sample in an inhomogeneous applied field can cause spurious effects in magnetization measurements [26] since in each scan the sample goes effectively through an ac-field cycle. For a 4 cm scan the maximum relative field variation for our system is 2×10^{-4}. We have performed measurements at various scan lengths (ranging from 3 to 6.8 cm) and various scan speeds and not observed any effect on the magnetization jumps. In addition, we have mounted the sample and a thermometer on a stationary sample holder and recorded the SQUID voltage as the temperature is varied. Figure 4 shows the SQUID voltage in 4.2 T for increasing and decreasing temperatures. The SQUID voltage shows long time drifts which are in part dependent on cooling and warming rates. However, the data display a small step near 83.8 K which is clearly seen when plotted relative to a linear extrapolation of the low temperature behavior (shown in the inset). The step occurs on cooling and warming, and its height of 40 mV is close to the expected value of 47 mV corresponding to a magnetization change of 0.3 G. We note the remarkable similarity of these data with those shown in Fig. 3. Since the long time drifts of the SQUID voltage are difficult to control, we take the data in Fig. 4 as proof of the existence of an inherent magnetization jump and rely for precise quantitative measurements on the conventional mode of operation of the magnetometer.

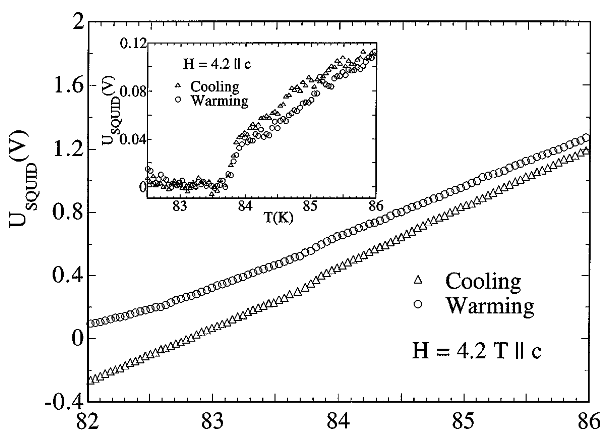

FIG. 4. Temperature dependence of the SQUID voltage in a field of 4.2 T on warming and cooling, with the sample stationary. The inset shows the jump of the SQUID voltage for increasing and decreasing temperatures.

The data from the resistivity and magnetization measurements are compiled in Fig. 5. The bottom panel shows the phase diagram as determined from the resistive drops in $\rho(T)$ and from the magnetization jumps in $M(H)$ and $M(T)$. The good coincidence of all three determinations underlines the conclusion that both the magnetization jumps and the resistivity drops are caused by the same first-order flux line lattice transition. The melting line is well described by a power law of the form $H_m(T) = 99.7\ (1 - T/T_c)^{1.36}$. Similar forms have been reported earlier [12,23]. The exponent observed here is close to that expected for a 3D XY critical point analysis, $2\nu = 1.33$. However, a critical point analysis appears incompatible with the first-order nature of the transition.

In the top panel on the left is shown the temperature dependence of the height of the magnetization jump as determined from $M(H)$ (squares) and from $M(T)$ (diamonds). The overall size of the magnetization jump observed here is similar to a previous report [23] and to that in $Bi_2Sr_2CaCu_2O_8$ [22]. The melting fields of $YBa_2Cu_3O_{7-\delta}$ are, however, much higher than in $Bi_2Sr_2CaCu_2O_8$ due to the much smaller anisotropy. Thus, in the present experiments only the high temperature region around T_c can be accessed. The maximum

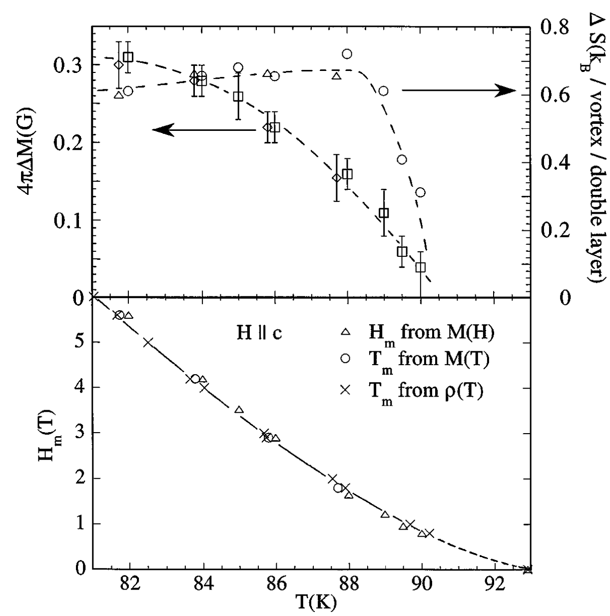

FIG. 5. Top panel: Temperature dependence of the magnetization jump, $4\pi\Delta M$, and the jump in entropy, ΔS. The dotted lines are guides to the eye. The results for the entropy have the same relative errors as the magnetization data. Error bars have been left off for clarity. Bottom panel: Phase diagram of the melting transition as determined from resistivity and magnetization measurements. At temperatures about 90 K there is no discontinuity in the magnetization detectable, and the dotted line represents a continuous extrapolation of the low temperature data towards T_c.

value of ΔM and a possible critical point of the melting line similar to that in $Bi_2Sr_2CaCu_2O_8$ [22] have not been located. Transport measurements [13] indicate that the sharp resistive feature associated with the first-order melting transition of $YBa_2Cu_3O_{7-\delta}$ crystal is suppressed in fields larger than 10 T. This field value will depend on the purity of the specific sample.

Using the Clausius-Clapeyron equation for a magnetic first-order transition, $dH_m/dT = -\Delta S/\Delta M$, the entropy jump per vortex per CuO_2 double layer in units of k_B is given by

$$\Delta S_V = -\frac{\Delta M}{H_m}\frac{dH_m}{dT}\frac{\phi_0 d}{k_B}.$$

Here, ϕ_0 is the flux quantum, $d = 11.7 \times 10^{-8}$ cm is the **c**-axis lattice constant, and k_B is the Boltzmann constant. (Since a magnetization of about 16 G is negligible as compared to an applied field of 42 kG, we assume throughout this paper that the internal magnetic field is uniform and equal to the applied field.) The results for the entropy jump are shown in the top panel on the right. The discontinuity of the entropy has an almost temperature independent value of about $(0.65k_B/\text{vortex})/CuO_2$ double layer at temperatures below 88 K and decreases rapidly towards zero at temperatures above 88 K. This value of $0.65k_B$ is of the same order as that obtained for $Bi_2Sr_2CaCu_2O_8$ [22]. Recent estimates of the size of the latent heat using Monte Carlo simulations give $(0.3k_BT_m/\text{vortex})/\text{double layer}$ for $YBa_2Cu_3O_{7-\delta}$ in a field of 10 T [3] and $(0.10k_BT_m/\text{vortex})/\text{double layer}$ [4], respectively, are somewhat smaller than the experimental results. In a calorimetric experiment the discontinuity of the entropy is expected to be visible through a temperature signal of the order of $\Delta T = \Delta ST_m/C$, where C is the total specific heat of the sample. At 84 K and 4 T this amounts to about 1.2 mK which is detectable in high resolution specific heat experiments [27]. However, up to now only large twinned crystals have been studied [27] where the melting transition is suppressed due to twin boundary pinning [12]. In addition, any broadening of the melting transition will reduce the temperature signal exponentially.

An interesting feature of the results in Fig. 5 is that ΔM and ΔS apparently go to zero near 90.5 K, well below the zero-field transition temperature. At the same time the resistive drops at T_m are broadened at temperatures above 90 K (i.e., field less than 1 T); see the inset of Fig. 3. A possible cause for this behavior is residual sample inhomogeneity which becomes relatively more important approaching T_c. Since the number of vortices decreases proportional to the field, single vortex pinning by the residual pinning centers can be expected to dominate the vortex behavior in the high temperature–low field region. This would suppress a collective first-order transition.

In conclusion, using moving- and stationary-sample SQUID magnetometry we have shown that an untwinned crystal of $YBa_2Cu_3O_{7-\delta}$ exhibits discontinuous jumps of the reversible magnetization. The location of the magnetization jumps in the H-T plane corresponds to that of the sharp drops of the resistivity and the onset of non-Ohmic behavior of the same sample. These results give proof to the existence of a first-order melting transition of the flux line system in untwinned $YBa_2Cu_3O_{7-\delta}$. The density of the flux line liquid is higher than that of the solid, as observed in $Bi_2Sr_2CaCu_2O_8$ [22]. The relative reduction of the average vortex spacing across the transition is about 4×10^{-6}. The latent heat associated with the transition amounts to $(0.65k_BT_m/\text{vortex})/CuO_2$ double layer at temperatures below 88 K and drops to zero rapidly at higher temperatures. We suggest that the temperature dependence of ΔM and ΔS near T_c is governed by sample inhomogeneities.

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