Resistive Upper Critical Field of $Tl_2Ba_2CuO_6$ at Low Temperatures and High Magnetic Fields

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The resistive upper critical field of overdoped single crystals of $Tl_2Ba_2CuO_6$ has been measured from the zero field transition temperature $T_c(0)$ (approximately 20 K) to temperatures as low as 12 mK, corresponding to less than $0.001T_c(0)$. In sharp contrast to the predictions of standard theories of superconductivity, the critical field is found to rise steeply with positive curvature as the temperature is reduced, and no sign of saturation is observed down to the lowest temperatures reached.

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One of the most striking and important properties of the cuprate superconductors is their high upper critical fields. These high fields have, however, posed an obstacle to the study of the field induced transition to the normal state at low temperatures, the nature of which remains a major unsolved problem.

In this paper we report measurements of this transition down to temperatures in the millikelvin range on single crystals of one of the cuprate materials, $Tl_2Ba_2CuO_6$, in which the critical field has been depressed to below 30 T. Samples with such low critical fields and zero field critical temperatures $T_c(0)$ of below 20 K were prepared by overdoping, i.e., increasing the hole-carrier concentration beyond that which produces the optimum T_c, via the addition of oxygen between the Tl-O bilayers. With increasing overdoping the temperature dependence of the resistivity changes gradually from linear (T) to quadratic (T^2) [1], and the resistive transition shifts, with only moderate changes in shape, monotonically down in temperature with increasing magnetic fields.

A similar behavior is observed in overdoped specimens of $La_{2-x}Sr_xCuO_4$ [2]. We note that underdoped or optimally doped cuprates exhibit resistivity profiles of a qualitatively different appearance. In contrast to the parallel shifts of overdoped samples, one observes a field induced broadening in which the field dependence of the top of the resistive transition is much weaker than that of the bottom [2–6].

At first sight, the more conventional appearance of the resistive transitions in the overdoped samples and the nearly quadratic temperature variation of the normal-state resistivities in zero field seem to suggest that these systems may be described as undergoing transitions from a conventional Fermi liquid to a BCS superconducting state. The present work on single crystals of overdoped samples of $Tl_2Ba_2CuO_6$ investigates this conjecture by means of studies of the transverse magnetoresistivity in fields of up to 18 T applied along the c axis at temperatures down to the millikelvin range.

Our results show that the resistive transition as a function of field shifts to higher fields as the temperature is reduced, *with no evidence of saturation down to the minimum temperatures reached, as low as 0.001 of* $T_c(0)$. This behavior is in sharp contrast with that expected on the basis of a naive application of the BCS model for the upper critical field.

The growth and detailed characterization of the structure and composition of the samples are described elsewhere [7]. Our $Tl_2Ba_2CuO_6$ crystals are tetragonal and, in agreement with other recent studies [8], are found to have approximately 7% of Tl sites occupied by Cu. This substitution, however, has surprisingly little effect on the carrier mean free path in the CuO_2 planes which, in the relaxation time approximation based on a two-dimensional Fermi surface of radius 0.6 $Å^{-1}$, is estimated to be of the order of 10^3 Å at low temperatures [9].

The transverse magnetoresistivity has been measured in five samples, with typical dimensions of 250 μm × 50 μm × 5 μm, and values of $T_c(0)$ varying between 6 and 22 K. The results in all samples are found to be qualitatively the same. The data collected for one of them, $S1$, are shown in Figs. 1–3.

Robust, low-resistance electrical contacts to the sample are essential to avoid excessive Joule heating at low temperatures and to provide adequate heat sinking to the mixing chamber of our dilution refrigerator. The contacts were made using Dupont 6838 epoxy annealed for a few minutes at 470 °C in an oxygen atmosphere and then quenched to room temperature. This procedure led to contact resistances of approximately 1 Ω at room temperature, typically falling by a factor of 5 by 20 K. The anneal time was short enough to leave the transition tem-

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perature unchanged.

The low temperature resistance measurements in the range 12 mK to 20 K were performed using a cryomagnetic system based on a top-loading dilution refrigerator and an 18.4 T superconducting magnet designed for low noise measurements of quantum oscillatory phenomena [10]. The samples were mounted in a miniature rotation mechanism, operating *in situ* in the tail of the dilution refrigerator, allowing precise alignment of the c axis parallel to the field. Thermal contact was made by electrically grounding one current lead of the sample to the mixing chamber, whose temperature was measured using calibrated Ge and RuO_2 thin film resistance thermometers. The resistivity in the a-b plane was measured via a standard four-terminal ac method. Joule heating of the sample at the current contacts was eliminated by measuring the current dependence of resistivity versus field curves at base temperature. At 12 mK the curves were independent of current only below 1 μA, and in practice a current of 0.1 μA was used below 100 mK. The voltage signal was detected using a shielded toroidal transformer mounted at 1 K, followed by a low noise room temperature preamplifier. The noise level was approximately 10^{-11} V. At higher temperatures, where Joule heating is no longer a problem, the resistance curves were found to be current independent from 0.1 to 100 μA (corresponding to current densities of 0.03 to 30 A/cm^2).

The temperature dependence of the resistivity of sample $S1$ in zero applied magnetic field is shown in Fig. 1. The resistivity near $T_c(0)$ varies from 10% to 90% of the normal-state value over a narrow range of approximately 1.8 K centered at 15 K. Three other samples studied had transition widths of between 1 and 1.5 K, while a fourth had a broader transition. Tiny variations, as small as 0.1%, in the oxygen concentration in the sample can lead to noticeable fine structure in the transition region. Large scale inhomogeneities which would grossly modify the transition region are, however, ruled out by the consistency of the basic results discussed below in different samples and in measurements on the same sample with fixed current contacts but two different sets of voltage contacts.

The normal-state resistivity in Fig. 1 can be fitted to a constant plus a term varying approximately as $T^{1.75}$, in agreement with measurements on samples with similar transition temperatures grown elsewhere [11]. The low values of the extrapolated residual resistivities of our samples, approximately 30–40 times lower than those at room temperature, are consistent, in the model discussed earlier, with very long mean free paths of the order of 10^3 Å. Although they are, in this sense, of exceptional quality, the extreme sensitivity of overdoped samples of $Tl_2Ba_2CuO_6$ to minute inhomogeneities in the oxygen concentration precludes a detailed description of the ideal form of the resistivity profile in the transition region. The overall shift of this region with magnetic field, which is largely insensitive to inhomogeneities on the scale described and is independent of the sample studied, will therefore be the focus of our attention.

As shown in Fig. 2, the resistive transition as a function of magnetic field broadens and shifts to higher fields as the temperature is lowered. The structure in the transition is similar to that in the zero field transition and is preserved at all temperatures. This behavior is observed in each of our samples, strongly suggesting that the finite zero field transition width gives one of the major contributions to the apparent field induced broadening.

The resistivity (ρ) in the saturated or flat portion of the ρ vs H curves (after the subtraction of a weak apparent normal-state magnetoresistance obtained by measurements above the zero field transition temperature) follows closely that expected from a smooth continuation to temperatures below $T_c(0)$ of the resistivity obtained in zero magnetic field (Fig. 1). This implies that the flat regions in the ρ vs H curves may be identified with the normal state (i.e., the state without long-range superconducting order).

Our results differ strikingly from those found in $YBa_2Cu_3O_7$ [3] and $Bi_2Sr_2CaCu_2O_8$ [4] which have high values of $T_c(0)$. They even differ from those found in

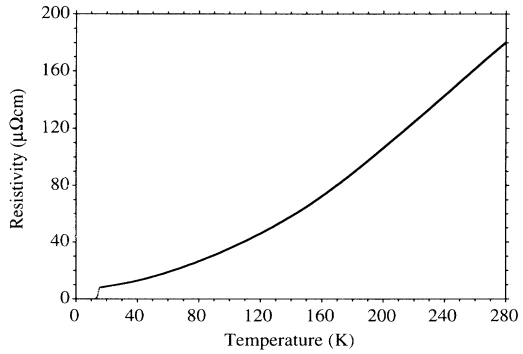

FIG. 1. Resistivity versus temperature in zero magnetic field for crystal $S1$.

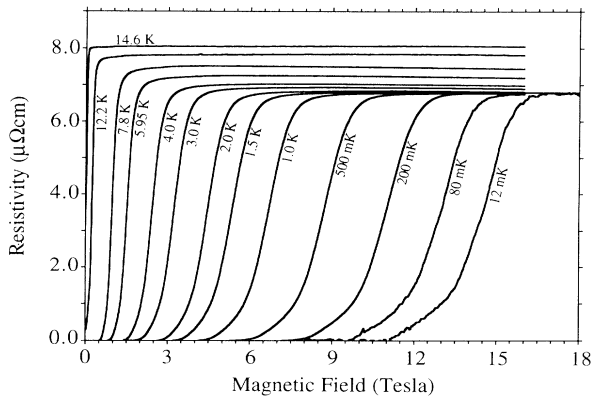

FIG. 2. The resistive transition of $S1$ as a function of magnetic field at various temperatures.

samples of $YBa_2Cu_3O_{7-x}$ in which $T_c(0)$ has been depressed by underdoping [6], and in optimally doped single crystals of $Bi_2Sr_2CuO_6$ [5], a system with a similar crystal structure to $Tl_2Ba_2CuO_6$ which exhibits low values of $T_c(0)$ of the order of 10 K (perhaps as a result of compositional or structural disorder) [12]. In all of these underdoped and optimally doped samples, the applied field is found to broaden the transition greatly (either as a function of applied field at a constant temperature or as a function of temperature in a constant applied field) and below 20 T the normal state can be accessed only at temperatures very close to $T_c(0)$.

For $Tl_2Ba_2CuO_6$, we may define a transition field $H^*(T)$ which satisfies the condition that $\rho(T,H^*)$ is equal to a fixed percentage f of the saturation (or normal-state) value at each temperature T [13]. The temperature variations of $H^*(T)$ for $f=10\%$, 50%, and 90%, with the 10% and 50% values normalized to that of 90%, are shown in Fig. 3. In all cases we find that $H^*(T)$ has a positive curvature and *continues to rise sharply with no sign of saturation down to temperatures as low as 0.001 of* $T_c(0)$. This key result of this paper is independent of the choice of f and of excitation current and was obtained for all the crystals that were studied.

The transition region may be expected to be broadened by spatial inhomogeneities in the superconducting order parameter arising from (i) static compositional variations or (ii) thermodynamic fluctuations, and (iii) by fluxoid flow in applied crossed electric and magnetic fields

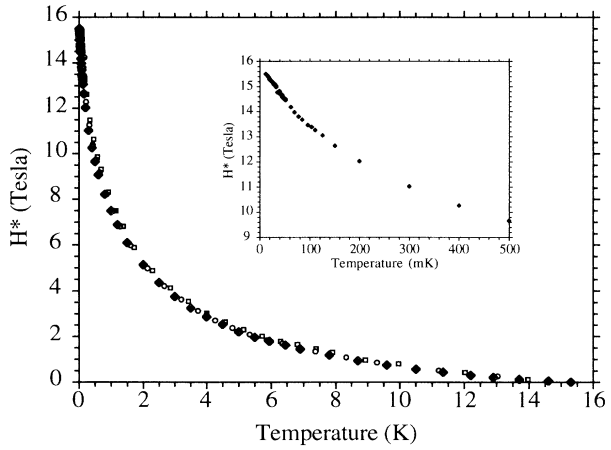

FIG. 3. The critical field $H^*(T)$ as defined in the text deduced from the resistivity measured at 90% (diamonds), 50% (open circles), and 10% (open squares) of the normal-state value at each temperature. Normalization constants have been applied to the temperature and field values for the 50% and 10% points to allow for the zero field transition width and the field broadening, to enable them to be plotted on the same axes. The values of the constants are 1.06 and 1.13 for the temperature values and 1.13 and 1.36 for the field values for the 50% and 10% points, respectively. The inset shows $H^*(T)$ vs T at low temperatures for the 90% measurements.

[14–17]. The importance for $Tl_2Ba_2CuO_6$ of (i) is discussed above, while (ii) and (iii) may be expected to be particularly significant in quasi-two-dimensional systems with short coherence lengths, particularly in high applied magnetic fields when the boson field for the Cooper pairs tends to exhibit a one-dimensional character. The intrinsic broadening in extreme cases may preclude the identification of a well-defined transition field, except perhaps at the point where macroscopic persistent currents first appear. Because of fluxoid flow in resistivity measurements, however, this does not in general correspond to the upper critical field H_{c2}, which, in simple cases, may be identified with the point at which the reversible diamagnetic magnetization exhibits a sharp change in slope. In the presence of strong fluctuations of the order parameter, however, even this point may not be well defined. In simple cases, at least, it is expected that the bottom of the resistive transition represents the "irreversibility line" (in the language of fluxoid flow), while H_{c2} is to be identified with some point near the top of the resistive transition [14–16] (although see also Ref. [17]). Reversible dc magnetization measurements tend to support this view for $YBa_2Cu_3O_7$ [18]. The key point is that $H_{c2}(T)$ as defined via the top of the resistive transition tends to rise so rapidly in most cuprate systems that its temperature dependence cannot be studied over a wide temperature range.

As already noted, the temperature dependence of $H^*(T)$ in $Tl_2Ba_2CuO_6$ is qualitatively similar both near the bottom and near the top of the resistive transition, and $\rho(H)$ does appear to saturate to the expected normal-state value just above the transition region. In this case it is natural to speculate that the temperature dependence of $H^*(T)$ is similar to that of $H_{c2}(T)$. Our identification of the temperature dependence of $H^*(T)$ with that of $H_{c2}(T)$ would seem to be especially plausible at low T where the thermally activated motion of fluxoids may be expected to be quenched. The absolute values of H^* are still below the paramagnetic limit, however, so we cannot rule out processes involving the quantum motion of fluxoids, for example.

A positive curvature of $H_{c2}(T)$ vs T plots has been reported in a number of other superconductors, including layer compounds [19], quasi-two-dimensional organic metals [20], the cubic bismuthates [21] and the "electron-doped" cuprates [22,23], and Fe-doped $YBa_2Cu_3O_7$ [24]. In most cases, however, measurements have been restricted to a range above 10% of $T_c(0)$ and in the few exceptions among layer materials studied to somewhat lower reduced temperatures, the $H_{c2}(T)$ curve is found to saturate.

In the conventional BCS picture, $H_{c2}(T)$ is linear in T near $T_c(0)$ and saturates in the zero temperature limit. A mild upward curvature can be produced within this model in the presence of strong impurity scattering [25], a limit which, in view of the high mean free paths in-

ferred earlier, is unlikely to be applicable to the material studied here. Another theoretical approach which leads to upward curvature has been reported by Alexandrov and co-workers, who considered the effect of a magnetic field on the Bose condensation of bosons which were assumed to have formed well above $T_c(0)$. A recent version of the theory, in which localization of bosons at low temperatures is postulated, leads to a form of $H_{c2}(T)$ which exhibits an upward curvature down to very low temperatures [26].

In general, thermodynamic fluctuations in the order parameter produce significant modifications of the prediction of the BCS mean field model in systems with small coherence lengths [27]. The effect of fluctuations may be expected to be increasingly important in high magnetic fields where the fluctuations become effectively one dimensional. The growth of the amplitude of the fluctuations with increasing field can lead to a progressively stronger suppression of $T_c(H)$ from the BCS value and, hence, to a transformation of the H_{c2} curve from one of negative to one of positive curvature.

This qualitative behavior is, particularly for a system with a short coherence length along the field direction, to be expected from a treatment of the coupling of fluctuations of the order parameter in the simplest Hartree approximation [28,29], in the presence of scattering from imperfections which lead to a *gradual* transformation to a one-dimensional limit at high field. Corrections to this model in the high field quasi-one-dimensional limit are likely to be important but they may not entirely alter the general qualitative form of the shift of the resistive transition region with temperature. The Bose condensation model discussed above can be viewed as an extreme limit, beyond the Hartree approximation, but in which the effects of reduced dimensionality and impurity scattering play a qualitatively similar role.

In conclusion, we have observed an anomalous temperature dependence of the resistive critical field $H^*(T)$ in $Tl_2Ba_2CuO_6$ which shows no evidence of saturation down to very low temperatures. Fluctuations of the order parameter in finite fields are evidently of great importance in this material but the precise way in which they are to be treated, especially at low temperatures, remains an incompletely solved problem.

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Note added.—Since submission of this Letter we have become aware of independent unpublished work by M. S. Osofsky and co-workers on Bi-Sr-Cu-O thin films in which very similar effects to those reported here have been observed.

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