Resistive upper critical field of thin films of underdoped $YBa_2(Cu_{0.97}Zn_{0.03})_3O_{7-\delta}$

D. J. C. Walker
Interdisciplinary Research Centre in Superconductivity, University of Cambridge, Madingley Road, Cambridge, CB3 OHE, United Kingdom
O. Laborde
Centre de Recherche sur les Très Basses Températures, Centre National de la Recherche Scientifique, 25 Avenue des Martyrs, 38042 Grenoble-cédex 9, France
and Centre de Recherche sur les Très Basses Températures, Laboratoire des Champs Magnétiques Intenses, CNRS, Boîte Postale 166, 38042 Grenoble-cédex 9, France
A. P. Mackenzie
Interdisciplinary Research Centre in Superconductivity, University of Cambridge, Madingley Road, Cambridge, CB3 OHE, United Kingdom
S. R. Julian
Cavendish Laboratory, University of Cambridge, Madingley Road, Cambridge CB3 OHE, United Kingdom
A. Carrington
Commissariat à l'Energie Atomique, Département de Recherche Fondamentale sur la Matière Condensée–SPSMS–LCP, 38054 Grenoble-cédex 9, France
J. W. Loram and J. R. Cooper
Interdisciplinary Research Centre in Superconductivity, University of Cambridge, Madingley Road, Cambridge, CB3 OHE, United Kingdom

(Received 1 August 1994; revised manuscript received 15 December 1994)

We report measurements of the magnetic-field dependence of the superconducting transitions of a series of underdoped $YBa_2(Cu_{0.97}Zn_{0.03})_3O_{7-\delta}$ thin films with transition temperatures (T_c) of 9.4, 12.5, 23, and 56.5 K. The *ab*-plane resistivity was measured in magnetic fields of up to 21 T applied both parallel and perpendicular to the *c* axis, at temperatures between 1.5 and 100 K, and for one sample down to 50 mK in fields of up to 16 T. The resistive critical field shows strong positive curvature all the way down to $0.006T_c$, similar to that observed previously for overdoped $Tl_2Ba_2CuO_{6+\delta}$ single crystals.

In most cuprate superconductors, the resistive transition from the normal to the superconducting state broadens significantly in an applied magnetic field.[1–3] The onset of the transition is hardly affected by the field, indicating that H_{c2} is very large, and there is a broad region of mixed state conductivity before zero resistance is reached. However for some compounds with sufficiently low transition temperatures T_c, it is possible to apply magnetic fields comparable with H_{c2}. In these circumstances a parallel shift is seen rather than a broadening, and the normal state resistivity can be recovered well below T_c.[4–8] This allows a resistive upper critical field H^* to be defined more easily, and H^* has a very unusual temperature dependence with positive curvature and a steep rise at low temperatures,[5,7] the origin of which is not understood.

Parallel shifts and unusual temperature dependences of H^* have been seen for two compounds which are heavily overdoped [$La_{2-x}Sr_xCuO_4$ (Ref. 4) and $Tl_2Ba_2CuO_{6+\delta}$ (Refs. 5 and 6)], for samples of $Bi_2Sr_2CuO_6$ whose exact doping level is not known,[7] and for electron-doped superconductors such as $Sm_{2-x}Ce_xCuO_4$.[8] It is of interest to study how the behavior of the resistive transition depends on the value of T_c, the doping level and on other factors which may be relevant. For example, specific heat measurements in zero magnetic field show that both $La_{2-x}Sr_xCuO_4$ and $Tl_2Ba_2CuO_{6+\delta}$ have very low superconducting condensation energies, and furthermore there is evidence for unpaired carriers at low temperatures, suggestive of pair breaking.[9]

In this work, our principal aim was to investigate the properties of a material in which T_c can be lowered by underdoping. For heavily underdoped or overdoped materials it is difficult to prepare samples with narrow resistive transitions in zero magnetic field, which is at least partly due to the stronger dependence of T_c on the doping level in these regions of the phase diagram. One obvious candidate for heavy underdoping is $YBa_2Cu_3O_{7-\delta}$ in which oxygen is removed from the Cu-O chains. An underdoped sample of $YBa_2Cu_3O_{7-\delta}$ displaying zero resistance at less than 20 K has been reported, but its transition is clearly very broad, even in zero applied field.[10]

In the present work, epitaxial thin films of $YBa_2Cu_3O_{7-\delta}$ doped with Zn were prepared and then underdoped by oxygen depletion. Zn substitutes for Cu atoms on the CuO_2 planes of $YBa_2Cu_3O_{7-\delta}$, and reduces T_c very rapidly.[11,12] In fully oxygenated samples, the normal state resistivity approximately obeys Matthiessen's rule, and the carrier concentration is thought to remain essentially unchanged.[13–15] The fully oxygenated 3% Zn films had the same T_c (56.5 K) as the corresponding ceramic samples. Removing oxygen gave samples with T_c below 20 K at $\delta \sim 0.3$. The low temperature resistivity in these samples is high ($\sim 400\ \mu\Omega$ cm), providing a second useful contrast with overdoped $Tl_2Ba_2CuO_{6+\delta}$, in which it is at least a factor of 50 lower.[5] On the other hand, the pair breaking and low condensation energy mentioned above are still present in Zn-doped $YBa_2Cu_3O_{7-\delta}$, so our experiment is probing the effects of reducing the doping level and shortening the electron mean free path on the unusual behavior of $H^*(T)$.

Surprisingly, we have observed similar behavior to that established previously for the overdoped materials, with the transition evolving from a broadening in a field to more of a shift as T_c is lowered. Furthermore, the temperature dependence of the resistive critical field for the lowest T_c sample shows positive curvature down to $0.006T_c$, similar to that previously reported for $Tl_2Ba_2CuO_{6+\delta}$.

The films were prepared by laser ablation from a 3% Zn doped polycrystalline sintered target of density 5.5 g/cm^3 onto $SrTiO_3$ substrates which were heated to 780 °C. After deposition, they were cooled to 470 °C in 1 atm of pure O_2, held for 20 mins and then cooled to room temperature in a further 20 mins. The as-grown films used in this study had resistive transition widths (10–90 %) of between 1 and 2.5 K. The zinc concentration was transferred accurately from target to film and was found to be homogeneous within the detection limits of electron microprobe analysis ($\pm 1.5\%$ of the total zinc concentration). The electron microprobe was also used to determine the film thickness, by studying the accelerating voltage dependence of x-ray emission from the film and substrate.[16] This gave absolute errors of $\pm 10\%$ and relative ones of $\pm 2\%$ in ρ. The technique used for oxygen removal has been described previously[17] and involves the samples being heated to high temperature in pure flowing oxygen and then quenched. Quench temperatures of 570 °C and 605 °C gave values for δ of approximately 0.26 and 0.30, respectively, and led to values of T_c of 23 and 12.5 K. These films were studied from 1.5 to 100 K in fields of up to 21 T, along with an as-grown sample ($\delta \sim 0.05$) with T_c of 56.5 K, and a further film with $T_c = 9.4$ K and a nominal δ value of 0.30 was studied down to 0.05 K.

The temperature-dependent resistivities of the three films used for the high field runs down to 1.5 K are shown in Fig. 1, with details of the transitions given in the inset. As oxygen is removed T_c drops and the normal state resistivity increases. The transitions of the lower T_c samples are rounded, with some excess conductivity to at least 10 K above the transition to "zero" resistance. This rounding is more apparent than for crystals of $Tl_2Ba_2CuO_{6+\delta}$ with similar values of T_c. In the present case, the normal state conductivity is much lower, which would highlight fluctuation effects, but we are unable to rule out oxygen inhomogeneity as the cause. This uncertainty leads to difficulty in interpreting the data in the applied magnetic fields both at the top of the transition and well into the normal state.

Figure 2 shows the behavior of the resistive transition as a function of temperature at a series of applied magnetic fields of up to 8 T applied parallel to the c axis of the films. For the fully oxygenated sample (A), all fields

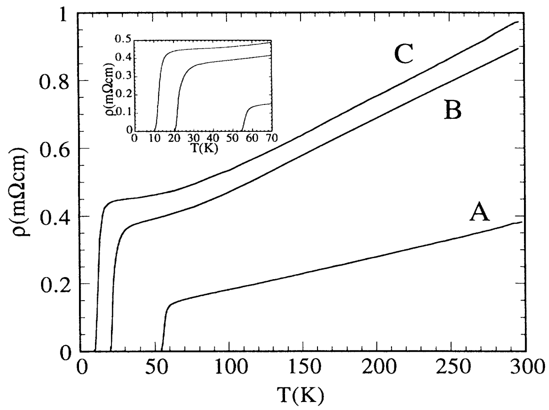

FIG. 1. The in-plane resistivity, ρ_{ab}, is plotted against temperature from 0 to 300 K for thin films of $YBa_2(Cu_{1-x}Zn_x)_3O_{7-\delta}$ with $\delta \sim 0.05$ (sample A), $\delta \sim 0.26$ (sample B) and $\delta \sim 0.30$ (sample C). The inset shows a close-up of the transitions.

simply broaden the transition, suggesting mixed state resistivity and a high value of H_{c2}, while for the oxygen depleted samples this broadening is seen only at low fields, higher fields producing a more parallel shift which probably reflects a strongly reduced H_{c2}. There is a pronounced positive magnetoresistance in the region where the zero field transition is rounded (approximately 25–35 K for sample B and 15–25 K for sample C).

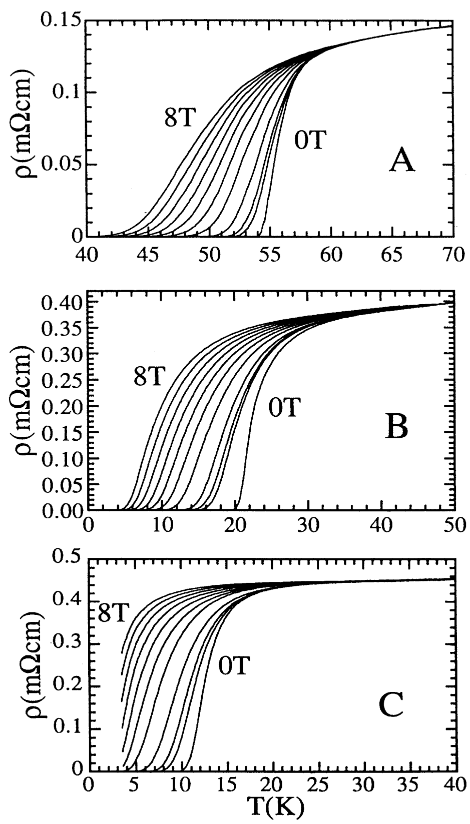

FIG. 2. The resistive transitions for all three samples with the fields of up to 8 Tesla applied parallel to the c axis (the field values are 0, 0.3, 0.5, 1, 2, 3, 4, 5, 6, 7, and 8 Tesla).

The results of a series of sweeps to high fields at constant temperature are shown in Fig. 3, and again there is a marked difference between the broadening shown by sample A and the tendency towards a shift shown by samples B and C. As a rule of thumb, the $\rho(T)$ curves near the 50% point become parallel when the application of the field has reduced T_c by a factor of 2. As expected, as T_c is lowered smaller fields are required to destroy superconductivity. For sample A, 21 Tesla causes hardly any observable resistance at $t=T/T_c=0.5$ but appears to restore the normal state even at $t=0.1$ for sample C.

The critical field anisotropies for the 12.5, 23, and 56.5 K samples were extracted from measurements with the field parallel and perpendicular to the c axis, and were found to be approximately 10.5, 8, and 5.5, respectively. These compare with approximately 5 for the most overdoped $La_{2-x}Sr_xCuO_4$ sample in Ref. 4 and approximately 35 for the overdoped $Tl_2Ba_2CuO_{6+\delta}$ sample in Ref. 6, for which the anomalous temperature dependence for the resistive critical field was originally found. So the field dependence of the resistive transitions does not seem to show any obvious correlation with the anisotropy.

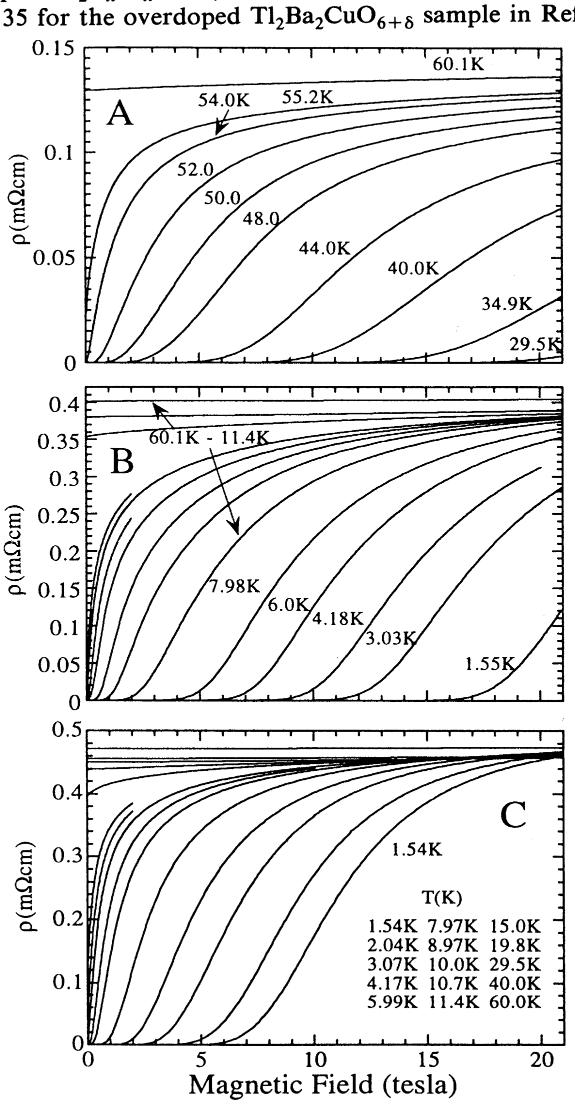

FIG. 3. The resistive transitions for all three samples plotted against applied magnetic field from 0 to 21 Tesla, with the field parallel to the c axis. For sample B, the temperatures between 11.4 and 60.1 K are 11.4, 13.9, 15.9, 17.8, 18.8, 19.8, 20.4, 29.5, 40.0, and 60.1 K.

As noted in Ref. 5, one of the features of a transition which shifts rather than broadens in an applied magnetic field is that no matter what criterion is chosen to define a resistive critical field H^*, the same basic temperature dependence is obtained if H^* is plotted against $t=T/T_c$, and t is obtained taking into account that there is a finite transition width in zero applied field.[18] If the transition broadens, different criteria lead to different temperature dependences for H^*. For sample A, whose transition does broaden, this is indeed the case, with the 10% criterion leading to a significantly more curvature for H^* vs t than the 50% criterion (not shown).

For the low T_c samples, the present case is slightly more complicated than the situation discussed in Ref. 5, for several reasons. Firstly, the rounding and high temperature tail of the transitions in zero field lead to some ambiguity in defining T_c, especially for the 90% resistance point. There are also difficulties in obtaining ρ_n at a given temperature and field, as it is large, and there is the possibility of localization, which could give unusual behavior at low temperatures and high fields. These complications all lead to greater uncertainty as the criterion is raised, so in Fig. 4 we only show the temperature dependence of H^* obtained from the 50% and 1% criteria with the 1% data scaled by a factor of 1.71. All three show the strong upward curvature observed in the overdoped materials, and they have a remarkably similar temperature dependence to that of $Tl_2Ba_2CuO_{6+\delta}$. This similarity was confirmed by measurements on another film (sample D), with $T_c=9.4$ K which was studied down to 50 mK in fields of up to 16 Tesla (solid circles in Fig. 4).

Several quite different interpretations of the unusual behavior of $H^*(T)$ have been proposed recently. It has been suggested that it may reflect the unusual properties

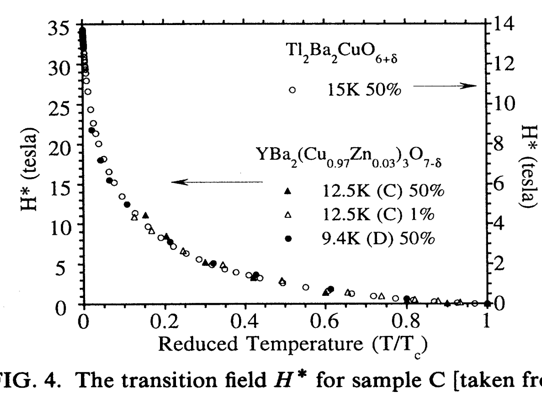

FIG. 4. The transition field H^* for sample C [taken from the data in Fig. 3(c)] is plotted against reduced temperature $t=T/T_c$. The data are plotted for the field at which the transition reaches 50% of the normal state resistivity with the data for the 1% point scaled by a factor of 1.71. The data for the 50% criterion (with H^* divided by a factor of 1.3) are also plotted for the fourth sample (D). On the right hand axis, $H^*(T)$ data are shown for the 50% criterion for the overdoped $Tl_2Ba_2CuO_{6+\delta}$ single crystals studied in Ref. 5.

of the normal state,[19] evidence for a bipolaron picture,[20] evidence for a low-energy scale and a very temperature-dependent effective mass[21] or even strong (almost critical) fluctuation effects.[22] The present work places constraints on all of the above theories since the unusual behavior is shown to be present on both the underdoped and overdoped sides of the phase diagram, in compounds for which the mean free path is shorter (the present work) or longer ($Tl_2Ba_2CuO_{6+\delta}$, Refs. 5 and 6) than the superconducting coherence length.

It is possible that the low-energy scale suggested in Ref. 21 could be linked with the linear term in the specific heat below T_c which is common to both materials. However the linear term also results in a low condensation energy which is the basis of the approach suggested in Ref. 22. A key question is whether the observed value of $H_{c2}(0)$ is enhanced over that expected for a conventional superconductor or not. In common with observations on other materials,[5-7] if we use the standard Werthamer-Helfand-Hohenberg (WHH) formalism based on $dH_{c2}(T_c)/dT$, we estimate $H_{c2}(0)$ to be less than 1 T for samples C and D, considerably less than that measured. A very low estimate of 0.7 T is also obtained from a simple estimate of the coherence length (ξ_0) in terms of the Fermi velocity and T_c. These estimates of $H_{c2}(0)$ strongly favor the temperature-dependent mass enhancement picture, but the very short mean free path in these Zn-doped films (~ 10 Å if $k_F \sim 0.6$ Å^{-1}) could cause ξ_0 to be considerably lower and $H_{c2}(0)$ to be correspondingly higher (15 T or more is possible). Thermodynamic measurements in a magnetic field (specific heat or magnetization) should help to resolve this issue.

In conclusion, we have shown that the qualitative behavior of the resistive transition in oxygen depleted, zinc doped $YBa_2Cu_3O_{7-\delta}$ is similar to that seen in oxygen rich $Tl_2Ba_2CuO_{6+\delta}$. As T_c is lowered, the transition behavior changes from a broadening to more of a shift, making it possible to define a resistive critical field H^* for the lowest T_c sample. In spite of the fact that $YBa_2(Cu_{0.97}Zn_{0.03})_3O_{7-\delta}$ differs greatly from $Tl_2Ba_2CuO_{6+\delta}$ in its doping level (heavily underdoped as opposed to heavily overdoped) and has a much higher normal state resistivity, H^* for the two compounds has a remarkably similar temperature dependence. These results suggest that a low T_c is of primary importance, but both compounds also have the common features of very low superconducting condensation energies and a linear term in the specific heat at low temperatures. Further work is needed to determine the precise relationship between these properties and the temperature dependence of H^*.

We acknowledge useful discussions with J. M. Wade. Samples A, B, and C were studied between 1.5 and 100 K in a 21 T Bitter magnet at the High Magnetic Field Laboratory, a joint CNRS/MPI facility in Grenoble. The 18 T superconducting magnet/dilution refrigerator system at the University of Cambridge was used for the low-temperature measurements on a fourth sample (D).

[1]R. J. Wijngaarden, K. Heeck, R. P. Griessen, A. A. Menovsky, and M. J. V. Menken, Physica C **153-155**, 1329 (1988).
[2]Y. Iye, T. Tamegai, T. Sakakibara, T. Goto, N. Miura, H. Takeya, and H. Takagi, Physica C **153-155** (1988).
[3]T. T. M. Palstra, B. Batlogg, L. F. Schneemeyer, and J. V. Waszczak, Phys. Rev. Lett. **61**, 1662 (1988).
[4]M. Suzuki and M. Hikita, Phys. Rev. B **44**, 249 (1991).
[5]A. P. Mackenzie, S. R. Julian, G. G. Lonzarich, A. Carrington, S. D. Hughes, R. S. Liu, and D. C. Sinclair, Phys. Rev. Lett. **71**, 1238 (1993).
[6]A. Carrington, A. P. Mackenzie, J. R. Cooper, and D. Sinclair, Phys. Rev. B **49**, (1994).
[7]M. S. Osofsky, R. J. Soulen, S. A. Wolf, J. M. Broto, H. Rakoto, J. C. Ousset, G. Coffe, S. Askenazy, P. Pari, I. Bozovic, J. N. Eckstein, and G. F. Virshup, Phys. Rev. Lett. **71**, 2315 (1993).
[8]I. W. Sumarlin, S. Skanthakumar, J. W. Lynn, J. L. Peng, Z. Y. Li, W. Jiang, and R. L. Greene, Phys. Rev. Lett. **68**, 2228 (1992).
[9]J. W. Loram, K. A. Mirza, J. M. Wade, J. R. Cooper, and W. Y. Liang, Physica C **235- 40**, 134 (1994).
[10]G. T. Seidler, T. F. Rosenbaum, D. L. Heinz, J. W. Downey, A. P. Paulikas, and B. W. Veal, Physica C **183C**, 333 (1991).
[11]J. M. Tarascon, P. Barboux, P. F. Miceli, L. H. Green, G. W. Hull, M. Eibschultz, and S. A. Sunshine, Phys. Rev. B **37**, 7458 (1988).
[12]G. Xiao, M. Z. Cieplak, D. Musser, A. Gavrin, F. H. Streitz, C. L. Chien, J. J. Rhyne, and J. A. Gotaas, Nature **332**, 238 (1988).
[13]J. R. Cooper, S. D. Obertelli, P. A. Freeman, D. N. Zheng, J. W. Loram, and W. Y. Liang, Supercond. Sci. Tech. **4**, S 277-279 (1991).
[14]T. R. Chien, Z. Z. Wang, and N. P. Ong, Phys. Rev. Lett. **67**, 2088 (1991).
[15]S. D. Obertelli, J. R. Cooper, and J. L. Tallon, Phys. Rev. B **46**, 22, 14 928 (1992).
[16]See, for example, A. P. Mackenzie, Rep. Prog. Phys. **56**, 557 (1993).
[17]A. Carrington, D. J. C. Walker, A. P. Mackenzie, and J. R. Cooper, Phys. Rev. B **48**, 13 051 (1993).
[18]Each criterion is the resistivity from the transition region expressed as a fraction of the normal state resistivity ρ_n extrapolated to that temperature and field. If the zero field transition has a finite width, the value of T_c used to calculate the reduced temperature t is obtained using the same criterion.
[19]R. G. Dias and J. M. Wheatley, Phys. Rev. B **50**, 13 887 (1994).
[20]A. S. Alexandrov, Phys. Rev. B **48**, 10 571 (1993).
[21]A. P. Mackenzie, S. R. Julian, C. T. Lin, and D. C. Sinclair, (unpublished).
[22]J. R. Cooper, J. W. Loram, and J. M. Wade, Phys. Rev. B **51**, 6179 (1995).