PHYSICAL REVIEW LETTERS

Anisotropic Superconducting Properties of $YBa_2Cu_3O_{7-\delta}$ ($\delta = 0.1$ and 0.4) Untwinned Single Crystals

W. Bauhofer, W. Biberacher,[a] B. Gegenheimer, W. Joss, R. K. Kremer, Hj. Mattausch, A. Müller, and A. Simon

Max-Planck-Institut für Festkörperforschung, D-7000 Stuttgart 80, Federal Republic of Germany and F-38042 Grenoble CEDEX, France

(Received 11 July 1989)

We have performed a detailed anisotropy study of the superconducting properties of untwinned single crystals of $YBa_2Cu_3O_{7-\delta}$ in magnetic fields up to 22 T using a rf method giving critical fields H^* determined by the onset of flux-line motion. For $\delta \approx 0.1$ we find the highest H^* along the b axis; the a-b anisotropy amounts to 20% at 85 K. The 60-K superconductivity for $\delta \approx 0.4$ is characterized by the largest H^* along the a axis and pronounced 2D behavior as manifested by a cusp in the angular dependence of H^* and by the extremely steep slope of $H^*(T)$ perpendicular to c. We discuss our experimental results with respect to the significance of the Cu-O chains for high-T_c superconductivity of $YBa_2Cu_3O_{7-\delta}$.

PACS numbers: 74.60.Ec, 74.70.Vy

The crystal structure of $YBa_2Cu_3O_{7-\delta}$ [$YBa_2(CuO_2)_2CuO_{3-\delta}$] contains copper and oxygen atoms in two different structural elements: CuO_2 planes parallel to the a-b plane and $CuO_{3-\delta}$ chains parallel to the b axis. Oxygen vacancies are exclusively located in the $CuO_{3-\delta}$ chains ($0 \le \delta \le 1$). For $\delta = 0.5$, full and empty chains with $\delta = 0$ and $\delta = 1$ are believed to alternate in the direction of the a axis.[1] The superconducting transition temperature shows as a function of δ two distinct plateaus, ≈ 90 K for $0 \le \delta \le 0.2$ and ≈ 60 K for $0.3 \le \delta \le 0.5$.[2] Since the structural changes for varying δ affect the chains only, the intrinsic anisotropy of the superconducting parameters measured for different values of δ should elucidate the relative significance of planes and chains for high-T_c superconductivity in $YBa_2Cu_3O_{7-\delta}$.

Measurements of the anisotropy of the upper critical field H_{c2} on $YBa_2Cu_3O_{7-\delta}$ single crystals are complicated by two facts. First, the usual resistivity and ac methods seem to measure an upper critical field H^* determined by the dissipation due to the onset of flux-line motion.[3-6] dc SQUID measurements of H_{c2} by Welp et al.[7] give values for $|dH_{c2}/dT|$ more than twice as large as those obtained by other methods. This result is in agreement with earlier Raman data by Ruf et al.[8] The dc magnetization curves are fully reversible over several kelvin below $T_c(H)$ and it was argued[4] that the values obtained by other methods indicate instead the points where the magnetization curves become irreversible. However, the anisotropy ratio $(dH_{c2,\perp c}/dT)/(dH_{c2,\parallel c}/dT) = 5.5$ as measured by Welp et al.[7] does not differ qualitatively from $(dH^*_{\perp c}/dT)/(dH^*_{\parallel c}/dT) = 6$ to 10.[9] Thus, the anisotropy of H^* is close to the anisotropy of the intrinsic H_{c2}. We have chosen a rf method in view of the small dimensions of our untwinned crystal. Our measuring frequency of $\approx 10^7$ Hz is still 2 orders of magnitude too low to give directly the intrinsic H_{c2}.[4] It should be noted that the sample used in the work by

Welp et al. had a volume 3000 times larger than our specimen.

The second problem is caused by the strong tendency of $YBa_2Cu_3O_{7-\delta}$ single crystals for twinning along [110] during the oxygen takeup upon cooling through the transformation from tetragonal to orthorhombic symmetry. However, single crystals with sizeable untwinned regions have been obtained by appropriate growth conditions. Optical reflectivity and Raman measurements[10-12] on such samples have been communicated. The absence of twinning has been proven by single-crystal x-ray analysis[13] which led to a composition of $YBa_2Cu_3O_{6.93(0.02)}$ for the investigated specimen. Here, we report measurements of H^* on a single-domain crystal of $YBa_2Cu_3O_{7-\delta}$ from the same batch. These measurements yield the anisotropy of H^* within the a-b plane. In addition, our angular-dependent H^* data for two different oxygen contents, $\delta \approx 0.1$ and 0.4, show that the 2D character becomes much more pronounced upon reducing the oxygen concentration from $YBa_2Cu_3O_{6.9}$ to $YBa_2Cu_3O_{6.6}$.

For the present investigation, a single-domain crystal of size $0.1 \times 0.12 \times 0.03$ mm^3 was selected. According to precession photographs this crystal was orthorhombic with lattice constants as given in Ref. 13. No sign of twinning was observed. The crystal had $T_c = 91.5$ K agreement with the value for δ refined from the single-crystal x-ray data. This sample will be referred to as $YBa_2Cu_3O_{6.9}$. After the measurements the same crystal was transformed to—still untwinned—$YBa_2Cu_3O_{6.6}$ with $T_c \approx 60$ K in the following way: The crystal was placed in a crucible formed from appropriate amounts of $YBa_2Cu_3O_{6.25}$ and $YBa_2Cu_3O_{6.75}$ which was heated in a quartz ampoule ($\sim 10\%$ excess volume compared with the crucible) to 770 K (70 h) and slowly cooled to 370 K within 80 h. After this treatment the crucible was analyzed as $YBa_2Cu_3O_{6.61}$ and appeared monophasic to x rays with lattice constants identical to those of the single
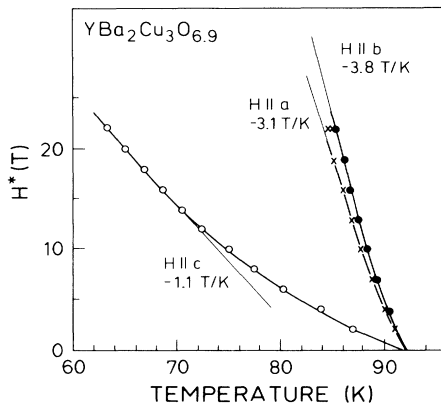
FIG. 1. Temperature dependence of H^* for an untwinned YBa$_2$Cu$_3$O$_{6.9}$ crystal oriented with the magnetic field parallel to the principal axes.

crystal and to YBa$_2$Cu$_3$O$_{6.62}$.[14] We refer to this sample as YBa$_2$Cu$_3$O$_{6.6}$.

For the measurements of T_c^* (defined by the onset of dissipation) the sample was inserted into a 50-turn coil (inner diameter ≈ 200 μm) of 12-μm isolated copper wire which was connected to a 150-pF capacitor to form a LC circuit resonant at 12 MHz. The transmission of this LC circuit was determined by a HP4194A gain-phase analyzer. Plotting the gain at resonance versus temperature usually resulted in a well-defined peak structure at the superconducting transition, allowing for a determination of T_c^* within an accuracy of ± 0.1 K. Only at high fields was a well resolved peak not obtained for the sample with $\delta \approx 0.4$. The change in slope of the gain was taken to determine T_c^* in this case. Analyses of the coil parameters show that the gain is mainly influenced by a variation of the resistive part of the ac susceptibility, in agreement with data reported by Worthington et al.[9]

The magnetic-field–dependent measurements were performed in a 25-T polyhelix magnet of the Grenoble High Field Facility. A two-axis rotating sample holder was used to orient the crystal with respect to the direction of the magnetic field. The possibility of accurately rotating the sample in any direction is essential for a determination of the a-b anisotropy, in order to exclude any influence of the strong suppression of T_c or H∥c. The positions with H⊥c were found by rotating the sample in the a-c and the b-c planes and could be determined within $\pm 0.2°$. The misalignment of H with respect to the a and b axes was within the order of $5°$.

Figure 1 shows the critical fields $H^*(T)$ for the three principal axes of YBa$_2$Cu$_3$O$_{6.9}$. All three curves exhibit a positive curvature near T_c. The slopes at the highest fields are -1.1 T/K for H∥c, -3.1 T/K for H∥a, and -3.8 T/K for H∥b. H^* is maximal along the crystal b axis; the anisotropy in the a-b plane at constant temperature amounts to 20%. The ratio of H^* parallel to the b
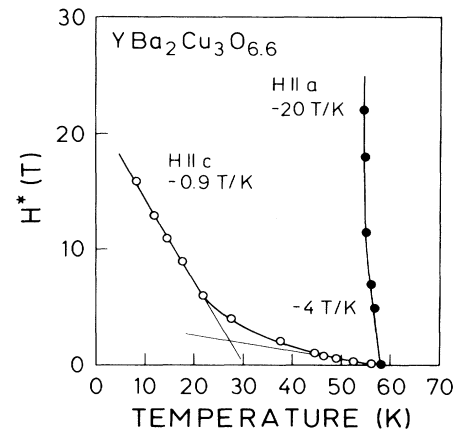

FIG. 2. Temperature dependence of H^* for an untwinned YBa$_2$Cu$_3$O$_{6.6}$ crystal oriented with the magnetic field parallel and perpendicular to the c axis. The curves for H∥a and H∥b are identical at this scale.

and to the c axes is about 7.7 at 85 K. The angular dependence of the critical temperatures at a constant field of 15 T is shown in Fig. 3, upper part.

In Fig. 2 we give the results for the same crystal subsequent to the change of the oxygen content to YBa$_2$Cu$_3$O$_{6.6}$. The anisotropy parallel to and perpendicular to the c axis has strongly increased; at 55 K, $H^*_{\perp c}/H^*_{\parallel c} = 40$. The upward curvature of H^* parallel to c is very pronounced. The determination of the anisotropy in the a-b plane is difficult due to the cusplike shape of $T_c^*(\theta)$ as is shown in Fig. 3, lower part. Our results show a slightly higher H^* along the a axis, opposite to
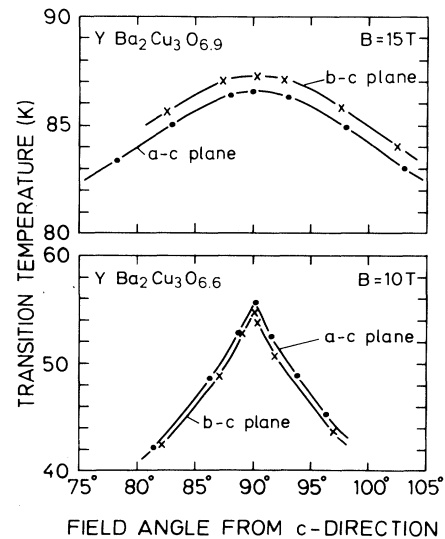

FIG. 3. Angular dependence of T_c^* for YBa$_2$Cu$_3$O$_{6.9}$ at $H = 15$ T (upper part) and for YBa$_2$Cu$_3$O$_{6.6}$ at $H = 10$ T (lower part), for rotations of H in the a-c and the b-c planes.

the case of the fully oxidized sample. The slopes of $H^*(T)$ in the a-b plane are higher than in the $YBa_2Cu_3O_{6.9}$ compound; the slope of H^* parallel to c near T_c is drastically reduced. The values of $-dH_{c2}/dT$ reported for ceramic samples with $YBa_2Cu_3O_{6.6}$, 0.35 T/K[15] and 0.41 T/K,[16] represent an average of our low-field and high-field data.

A delicate problem is the question of whether the strong positive curvature found for H^* over the whole temperature range is also an intrinsic property of H_{c2}. Welp et al.[7] claim that H_{c2} is linear near T_c; Fang et al.[17] even find a negative curvature. On the other hand, our results are very similar to results found for other highly anisotropic systems like intercalation compounds of TaS_2,[18] or the organic superconductor $(ET)_2Cu(SCN)_2$, where ET represents bis(ethylene-dithio)tetrathiafulvalene and SCN is thiocyanate.[19] Thus, a positive curvature seems to be a common feature of all highly anisotropic superconductors and not a special property of high-T_c material. Our results for H^* of the $YBa_2Cu_3O_{6.9}$ sample are in good agreement with other studies on twinned crystals of this compound.[9] We can therefore conclude that twin boundaries are not significant for the occurrence of high-T_c superconductivity. The effect of the twin boundaries on the flux-line motion remains unclear in view of the negative curvature of $H_{c2}(T)$ observed by Fang et al.[17] on highly oriented twinned samples.

Generally, there exists no simple relation connecting H^* with the corresponding H_{c2}. Welp et al. reported for $H = 5$ T perpendicular to c a decrease in T_c of 1.1 K. At the same field strength we find for H∥b, $\Delta T^* = -1.5$ K and for H∥a, $\Delta T^* = -1.9$ K. Thus, our anisotropic irreversibility lines $H^*(T)$ are rather close to $H_{c2}(T)$, and it does not seem very likely that the anisotropy changes qualitatively when increasing the frequency to measure the intrinsic H_{c2}. Presuming that the above arguments hold we can infer some considerations concerning the significance of CuO_2 planes and $CuO_{3-\delta}$ chains for high-T_c superconductivity in $YBa_2Cu_3O_{6.9}$. If the superconductivity were restricted to the planes only, the highest H_{c2} might be expected for H∥a because b is 2% larger than a, leading to a reduction of the overlap of the Cu-O wave functions and of the coherence length ξ_b in the b direction. Our result, that H^* is maximal for H∥b (suggesting $\xi_b > \xi_a$), lends some support to the idea that the chains take part in the 90-K superconductivity and do not merely serve as a hole reservoir.[20,21] Band-structure calculations for $YBa_2Cu_3O_{7-\delta}$ show that both planes and chains contribute to the electron density of states at the Fermi energy.[22]

The situation is different for $YBa_2Cu_3O_{6.6}$. The steep slope of H^* perpendicular to c implies that $-dH_{c2}/dT$ is more than twice as high for the 60-K superconductor as for the 90-K material. In addition, the slope of H^* parallel to c is drastically reduced near T_c, which leads

to a strong increase of the anisotropy parallel and perpendicular to the CuO_2 planes. This behavior can be explained with the assumption that for lower oxygen content the chains can no longer effectively couple the superconductivity of adjacent CuO_2-Y-CuO_2 blocks. The fact that $H^*(a) \geq H^*(b)$ further supports the idea that the chains have lost their significance for the conduction properties of $YBa_2Cu_3O_{6.6}$. The cusp observed in the $T_c^*(\theta)$ curve for H^* perpendicular to c [see Fig. 3, lower part; a similar angular dependence has been found for the extremely anisotropic $Bi_{2.2}CaSr_{1.9}Cu_2O_{8+x}$ (Refs. 23 and 24)] is another strong indication of a 2D system, in the manner of the angular dependence of H_{c2} for thin films given by Tinkham.[25] Additional support for the 2D character of the 60-K superconductor is supplied by the greater pressure dependence of T_c (in comparison with the 90-K case[26]) and the identification of nonmetallic Cu sites on the chain positions.[27]

Finally, we want to address the issue of "dimensional crossover" discussed by Klemm et al.[28] for layered compounds with weak Josephson coupling between the layers. A transition from 3D to 2D behavior is expected upon lowering the temperature to the point where the coherence length perpendicular to the layers becomes comparable with the layer distance. The crossover is expected to produce a characteristic upward curvature. The Ginzburg-Landau coherence lengths ξ can be calculated using the relations $\xi_{ab}^2 = \Phi_0/2\pi H_{c2,\parallel c}$ and $\xi_c/\xi_{ab} = H_{c2,\parallel c}/H_{c2,\perp c}$ (ξ_{ab} is parallel to the a-b plane and ξ_c is parallel to the c axis). Assuming that the anisotropy $H_{\parallel c}^*/H_{\perp c}^*$ is again comparable with the corresponding anisotropy of H_{c2}—as was found for $\delta \approx 0.1$—the substitution of H_{c2} in the above relations by H^* yields upper limits for ξ_{ab} and ξ_c. For the 60-K superconductor we obtain $\xi_c \leq 6$ Å at 55 K. This value is close to the crossover condition $\xi_c = s\sqrt{2}$ when s is taken as 8.3 Å corresponding to the distance between adjacent CuO_2-Y-CuO_2 blocks. We believe that this crossover can be seen in our data for H^* perpendicular to c where we observe a change in slope around 55 K (Fig. 2).

In conclusion, we have performed a complete anisotropy study of H^* for untwinned single crystals of $YBa_2Cu_3O_{7-\delta}$ with $\delta \approx 0.1$ and 0.4. Our measurements should help to elucidate the significance of the $CuO_{3-\delta}$ chains for the 90-K superconductivity. The results can be explained by assuming that for $\delta \approx 0.1$ the chains act as a coupling between adjacent superconducting CuO_2-Y-CuO_2 blocks. For the oxygen-deficient sample with $\delta \approx 0.4$ this coupling is strongly depressed, resulting in a pronounced 2D behavior for the 60-K superconductivity.

(a)Present address: Walther-Meissner-Institut, D-8046 Garching, Federal Republic of Germany.

[1]R. M. Fleming, L. F. Schneemeyer, P. K. Gallagher, B. Batlogg, L. W. Rupp, and J. V. Waszczak, Phys. Rev. B 37, 7920 (1988).

[2]R. J. Cava, B. Batlogg, C. H. Chen, E. A. Rietman, S. M. Zahurak, and D. Werder, Nature (London) 329, 423 (1987).

[3]A. Khurana, Physics Today, 42, No. 3, 17 (1989).

[4]A. P. Malozemoff, T. K. Worthington, Y. Yeshurun, F. Holtzberg, and P. H. Kes, Phys. Rev. B 38, 7203 (1988).

[5]Y. Yeshurun and A. P. Malozemoff, Phys. Rev. Lett. 60, 2202 (1988).

[6]C. Rossel, Y. Maeno, and I. Morgenstern, Phys. Rev. Lett. 62, 681 (1989).

[7]U. Welp, W. K. Kwok, G. W. Crabtree, K. G. Vandervoort, and J. Z. Liu, Phys. Rev. Lett. 62, 1908 (1989).

[8]T. Ruf, C. Thomsen, R. Liu, and M. Cardona, Phys. Rev. B 38, 11 985 (1988).

[9]T. K. Worthington, W. J. Gallagher, D. L. Kaiser, F. H. Holtzberg, and T. R. Dinger, Physica (Amsterdam) 153–155C, 32 (1988).

[10]C. Thomsen, M. Cardona, B. Gegenheimer, R. Liu, and A. Simon, Phys. Rev. B 37, 9860 (1988).

[11]J. Tanaka, K. Kamiya, and S. Tsurumi, Physica (Amsterdam) 153–155C, 653 (1988).

[12]F. Slakey, S. L. Cooper, M. V. Klein, J. P. Rice, and D. M. Ginsberg, Phys. Rev. B 39, 2781 (1989).

[13]A. Simon, J. Köhler, H. Borrmann, B. Gegenheimer, and R. Kremer, J. Solid State Chem. 77, 200 (1988).

[14]R. Flükiger, T. Müller, W. Goldacker, T. Wolf, E. Seibt, I. Apfelstedt, H. Küpfer, and W. Schauer, Physica (Amsterdam) 153–155C, 1574 (1988).

[15]D. Shi, J. Appl. Phys. 64, 4624 (1988).

[16]G. Fuchs, A. Gladun, R. Mueller, M. Ritschel, G. Krabbes, P. Verges, and H. Vinzelberg, J. Less-Common Met. 151, 103 (1989).

[17]M. M. Fang, V. G. Kogan, D. K. Finnemore, J. R. Clem, L. S. Chumbley, and D. E. Farrell, Phys. Rev. B 37, 2334 (1988).

[18]R. V. Coleman, G. K. Eiserman, S. J. Hillenius, A. T. Mitchell, and J. L. Vicent, Phys. Rev. B 27, 125 (1983).

[19]K. Oshima, H. Urayama, H. Yamochi, and G. Saito, Physica (Amsterdam) 153–155C, 1148 (1988).

[20]A. Simon, Angew. Chem. Int. Ed. Engl. 26, 579 (1987).

[21]S. I. Park, C. C. Tsuei, and K. N. Tu, Phys. Rev. B 37, 2305 (1988).

[22]J. Zaanen, A. T. Paxton, O. Jepsen, and O. K. Andersen, Phys. Rev. Lett. 60, 2685 (1988).

[23]M. J. Naughton, R. C. Yu, P. K. Davies, J. E. Fischer, R. V. Chamberlin, Z. Z. Wang, T. W. Jing, N. P. Ong, and P. M. Chaikin, Phys. Rev. B 38, 9280 (1988).

[24]D. E. Farrell, S. Bonham, J. Foster, Y. C. Chang, P. Z. Jiang, K. G. Vandervoort, D. J. Lam, and V. G. Kogan, Phys. Rev. Lett. 63, 782 (1989).

[25]M. Tinkham, Phys. Lett. 9, 217 (1964).

[26]C. W. Chu, Z. J. Huang, R. L. Meng, L. Gao, and P. H. Hor, Phys. Rev. B 37, 9730 (1988).

[27]W. W. Warren, Jr., R. E. Walstedt, G. F. Brennert, R. J. Cava, B. Batlogg, and L. W. Rupp, Phys. Rev. B 39, 831 (1989).

[28]R. A. Klemm, A. Luther, and M. R. Beasley, Phys. Rev. B 12, 877 (1975).