Direct Observation of Electronic Anisotropy in Single-Crystal $Y_1Ba_2Cu_3O_{7-x}$

T. R. Dinger, T. K. Worthington, W. J. Gallagher, and R. L. Sandstrom
IBM Thomas J. Watson Research Center, Yorktown Heights, New York 10598

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We report direct observation of the anisotropic electronic behavior of the high-temperature superconductor $Y_1Ba_2Cu_3O_{7-x}$. Critical-field and critical-current measurements performed on single crystals show anisotropies of 10 and greater. Critical supercurrent densities in favorable directions in single crystals are 3×10^6 A/cm^2 in low fields at 4.5 K and remain above 10^6 A/cm^2 to beyond 40 kG.

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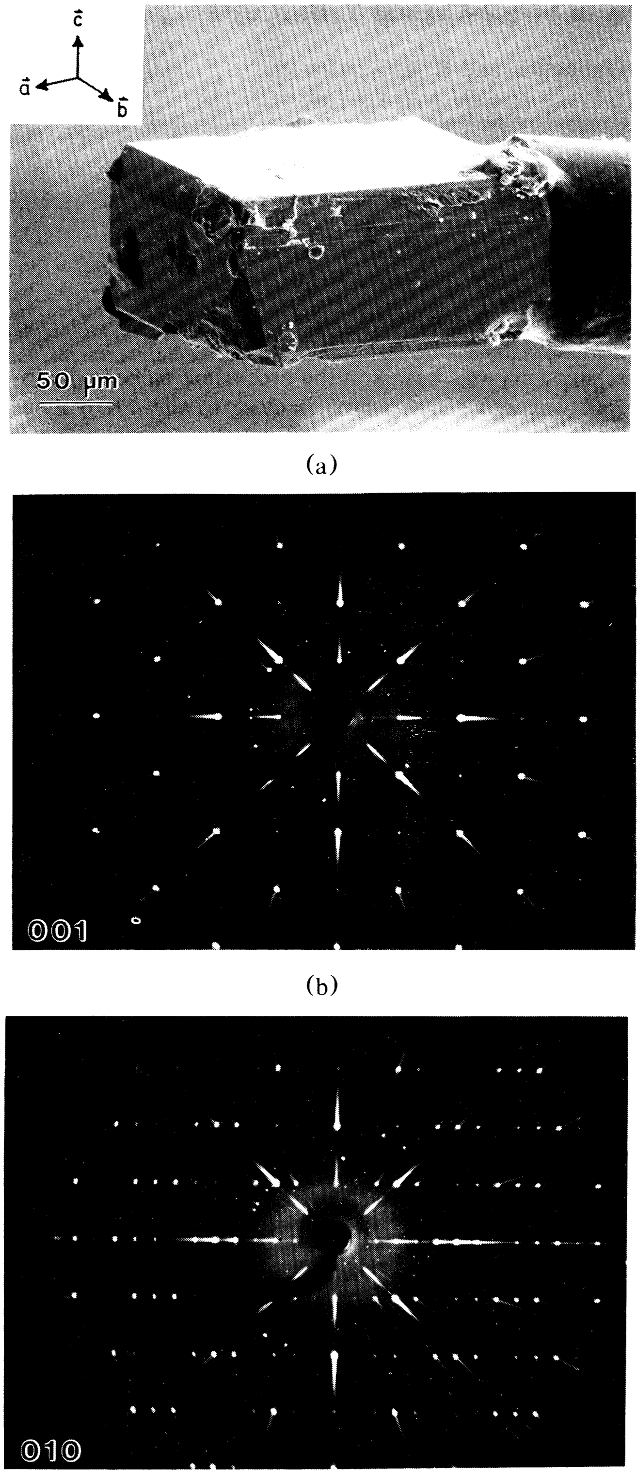
Feverish activity on high-T_c superconductivity in Cu-O–based perovskite-type materials has followed the breakthrough discovery of superconductivity at ~35 K in $La_{2-x}Ba_xCuO_4$ by Bednorz and Müller.[1] A highlight of this activity was the attainment of superconductivity at ~95 K, first achieved by Wu *et al.*[2] in mixed-phase compositions of Y-Ba-Cu-O, and the later isolation of $Y_1Ba_2Cu_3O_{7-x}$ as the superconducting phase.[3-5] The commonality of Cu-O layers to both the K_2NiF_4 structure of $La_{2-x}Ba_xCuO_4$ superconductors and the layered perovskite $Y_1Ba_2Cu_3O_{7-x}$ compounds suggests strongly that these two-dimensional layers are tied to the attainment of high transition temperatures. Indeed, Hidaka *et al.*[6] recently reported upper-critical-field anisotropies of 5 in single crystals $La_{2-x}Ba_xCuO_4$ and thus confirmed the anisotropic nature of the superconductivity in the $\simeq$35–40-K based superconductors. In this Letter we report the observation of even larger anisotropies in lower critical field and in the critical current density of single crystals of $Y_1Ba_2Cu_3O_{7-x}$. Furthermore, our measurements demonstrate that $Y_1Ba_2Cu_3O_{7-x}$ can carry large supercurrent densities ($\simeq 3\times10^6$ A/cm^2) in favorable directions at 4.5 K, and that the large supercurrent-carrying capability can persist in modest fields.

Single crystals of $Y_1Ba_2Cu_3O_{7-x}$ were grown by a technique similar to that used by Iwazumi *et al.*[7] for $La_{1.85}Sr_{0.15}CuO_4$. A sintered powder containing three phases, $Y_1Ba_2Cu_3O_{7-x}$, CuO, and $BaCuO_2$, and having a nominal composition in the molar ratio (0.125 Y_2O_3):(0.61 BaO):(1.00 CuO), was formed into a 1.27-cm-diameter pellet and fired in a slightly reducing atmosphere at 975 °C for 12 h. During the 975-°C soak, an oxidizing atmosphere was introduced to promote growth of the $Y_1Ba_2Cu_3O_{7-x}$ crystallites already present in the particle compact. This technique routinely produced highly faceted crystals with dimensions of approximately 200 μm (Fig. 1) with occasional crystals approaching 0.5 mm in size.[8] Precession-camera x-ray results (Fig. 1) using Mo radiation ($\lambda = 0.71069$ Å) showed the crystals to be of high quality with unit-cell dimensions of $a = 3.88$ Å and $b = 3.84$ Å given by the $a^* \times b^*$ net in Fig. 1. Rotation of the crystal by 90° gave the $a^* \times c^*$ net of Fig. 1 showing the three-layer modulation of the structure in [001] with $c = 11.63$ Å. The degree of orthorhombism of the single crystals based on the precession-camera photograph was $a/b = 1.01$ which is close to the 1.016 measured by Beyers *et al.*[9] Twinning of the crystals was not observed either optically or in the single-crystal diffraction experiment although transmission electron microscopy of similar crystals showed large amounts of twinning after the mechanical grinding used in the specimen preparation.[10] This result suggests that the crystals are unstable to mechanical stress and deform through the twinning process in order to minimize their strain energy. Such behavior has been previously noted and well documented in other ceramics such as $BaTiO_3$ and ZrO_2.[11,12]

We characterized our crystals by performing extensive magnetic measurements using a SHE 905 magnetometer equipped with a 40-kG superconducting solenoid. As grown, our crystals typically displayed superconducting diamagnetic transitions in the 40–50-K region. Annealing in flowing oxygen for extended periods at 450 to 500 °C raised the transition temperatures to $\simeq$85 K. Extensive measurements were performed on two 85-K crystals. One had dimensions $\simeq 400\times370\times120$ μm^3; the other had dimensions $\simeq 300\times300\times180$ μm^3. The larger crystal was the same one used in point-contact tunneling studies that indicated essentially no difference in the superconducting energy gap as determined from tunneling into different orientations of the crystal from a probe tip dug $\simeq$1000 Å into the crystal surface.[13]

We first investigated the low-field magnetization of our crystals with the field applied both parallel to and perpendicular to the Cu-O planes. The zero-field–cooled diamagnetism in several crystals in low fields (20 G) was essentially 100% after correction for demagnetizing factors. The Meissner flux expulsion expressed as a fraction of the diamagnetic shielding was small, varying from $\simeq$4% in the parallel orientation to $\simeq$17% in the perpendicular orientation. The 100% diamagnetic shielding is as expected; the low Meissner effect is somewhat surprising, although not without precedent. For example, small Meissner fractions in single crystals were observed some time ago in single crystals of $TaS_2(pyridine)_{1/2}$,[14] and more recently they were observed in single crystals of $La_{1.85}Sr_{0.15}CuO_4$.[9] Incomplete Meissner effects are generally associated with inhomogeneities in superconduct-



(a)

(b)

(c)

FIG. 1. Secondary-electron image and [001] and [010] zone-axis precession-camera photographs of a $Y_1Ba_2Cu_3O_{7-x}$ single crystal after extraction from the crystal mass. The [010] pattern shows the three-layer stacking of the perovskite blocks along [001].

ing materials. In doped materials, such as $La_{2-x}Sr_xCuO_4$, concentration variations are a likely source of inhomogeneities. In $Y_1Ba_2Cu_3O_{7-x}$ the inhomogeneities might be variations in the oxygen-defect ordering. Our crystals, with T_c slightly below the 92–95-K maximum achieved for $Y_1Ba_2Cu_3O_{7-x}$, likely possess some imperfections in the defect ordering. We are not yet sure of the significance of the difference in Meissner fractions between the parallel and perpendicular orientations.

Studies of magnetization hysteresis as an applied field is swept allow the determination of the lower critical field and provide a noncontact way of determining critical density from the magnetic moment resulting from induced screening currents. Antonova, Medvedev, and Shebalin[15] used such measurements to study the critical field and critical current anisotropy in $NbSe_2$ and we found the technique to work well for $Y_1Ba_2Cu_3O_{7-x}$.

Figure 2 shows magnetic hysteresis loops at 4.5 K for the larger crystal mounted with the Cu-O planes perpendicular to the field lines [Fig. 2(a)] and parallel to the field lines [Fig. 2(b)]. The differences in the scale and in the shape of the magnetization for the two orientations are very striking. The lower critical fields, $H_{c1}^{\perp}$ and $H_{c1}^{\parallel}$, for crystals oriented such that the applied field is perpendicular and parallel to the Cu-O planes, respectively, can be determined from the point in the initial part of each loop at which the departure from linearity begins. The departures occur at fields of 4 kG for the perpendicular orientation and at 600 G for the parallel orientation. Corrected for the demagnetizing factors we get $H_{c1}^{\perp}=8$ kG and $H_{c1}^{\parallel}=800$ G, giving a ratio of 10. This large lower-critical-field anisotropy was cross checked by measurements on a second crystal. In this case we repeatedly cycled the low-field magnetization curve to find the lowest field at which the magnetization was not reversible. This procedure yielded values of $H_{c1}^{\perp}=5.2$ kG and $H_{c1}^{\parallel}\lesssim 530$ G for this crystal, again giving a ratio of 10.

The difference in the magnitudes of the hysteresis in the two loops in Fig. 2 is even larger. In the perpendicular orientation the gradual departure of the magnetization curve from perfect diamagnetism indicates that there is strong pinning. In contrast, the sharp break at $H_{c1}^{\parallel}$ in the parallel orientation is indicative of weak pinning. According to the critical-state model of Bean[16] applied to a disk-shaped sample in an applied field H_a much in excess of the magnetization, the magnitude of the critical current density is related to the magnetization by the simple relation[17] $J_c=30M/r$, where M is the magnetization in electromagnetic units per cubic centimeter, r is the disk radius in centimeters, and J_c is the critical current density in amperes per square centimeter. We use this relationship and approximate r as the geometric mean of half of the sample dimensions perpendicular to the field. From the peaks in the 4.5-K magnetization curves, we estimate the maximum critical current densities in the two directions as $J_c^{\perp}=2.9\times 10^6$ A/cm^2

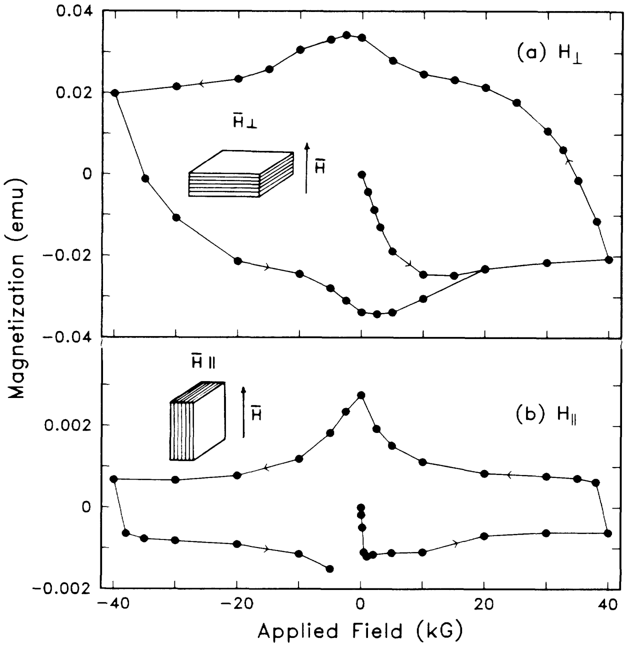


FIG. 2. Magnetization hysteresis loops at 4.5 K for a single crystal of $Y_1Ba_2Cu_3O_{7-x}$ with the Cu-O planes oriented (a) perpendicular to the applied magnetic field and (b) parallel to the applied field.

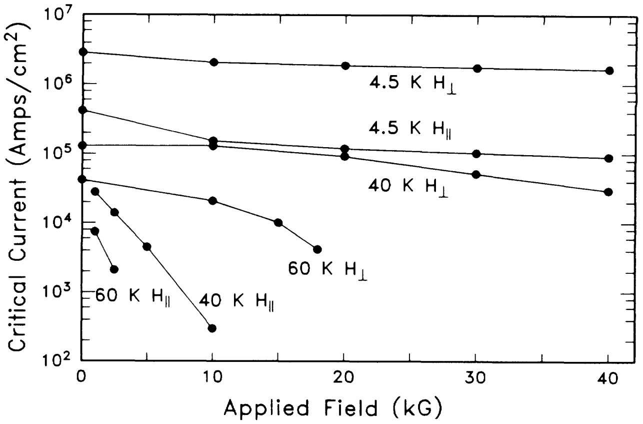


FIG. 3. Critical current densities deduced from magnetization hysteresis at various temperatures as a function of magnetic field applied either parallel or perpendicular to the Cu-O planes.

and $J_c^{\parallel} = 4.2 \times 10^5$ A/cm^2. (Note that our nomenclature is such that $J_c^{\parallel}$ is the critical current inferred from fields applied parallel to the Cu-O planes such that the induced screening currents actually flow perpendicular to the planes and $J_c^{\perp}$ is the critical current determined from currents induced along the direction of the planes by fields applied perpendicular to the planes.) In Fig. 3 we show the field and temperature dependence of the critical current density as determined from the hysteresis curves in Fig. 2 and similar curves taken at higher temperatures. From this plot one can see that the falloff of critical current density with applied field is not too severe. At 40 kG, $J_c^{\perp} = 1.7 \times 10^6$ A/cm^2 and $J_c^{\parallel} = 9.2 \times 10^4$ A/cm^2. The falloff with temperature is much more rapid. By 40 K in zero field, the perpendicular critical current density $J_c^{\perp} = 1.3 \times 10^5$ A/cm^2 and by 60 K this has fallen to $J_c^{\perp} = 4.2 \times 10^4$ A/cm^2. The critical-current anisotropy increases considerably at higher temperatures and fields.

Measurements taken on a second crystal at 4.5 K confirmed the same general anisotropic critical-current behavior, giving approximately three times greater anisotropy at zero field ($J_c^{\perp} = 3.2 \times 10^6$ A/cm^2 and $J_c^{\parallel} = 1.6 \times 10^5$ A/cm^2) and still larger critical-current anisotropies in larger fields. For instance, at 20 kG, $J_c^{\perp} = 2.2 \times 10^6$ A/cm^2 and $J_c^{\parallel} = 3.2 \times 10^4$ A/cm^2, for a ratio of 70. We observed in the course of these measurements that the hysteresis curves were extremely sensitive to slight misalignments from the parallel orientation. An estimated 5° misalignment of the crystal reduced the inferred critical-current anisotropy at 20 kG by more than an order of magnitude. It is possible that the smaller anisotropy observed in the first crystal was due to some slight misalignment, but we cannot rule out the possibility that it was a less perfect crystal.

Above H_{c1} we observed a slow time-dependent change in the magnetization similar to that observed in $La_{2-x}Ba_xCuO_4$ by Müller, Takashige, and Bednorz.[18] The magnetization was seen to change by as much as 20% and the time dependence was consistent with logarithmic behavior for times longer than 1000 min. For practical reasons, the magnetization points reported in this paper were typically taken a few minutes after establishing the field.

These critical-current and lower-critical-field measurements prove that the $Y_1Ba_2Cu_3O_{7-x}$ superconductor is strongly anisotropic with the good conducting directions being along the Cu-O planes. Refined structural analyses[19] show that there are one-dimensional Cu-O chains in the $Y_1Ba_2Cu_3O_{7-x}$ structure as well as two-dimensional Cu-O planes. Band-structure calculations[20] indicate that both one-dimensional and two-dimensional features may be making contributions to the high-transition-temperature superconductivity. However, it seems unlikely to us that the large supercurrents that we have observed at low temperatures could be carried by the one-dimensional chains.

From studies of intercalation superconductors, much is known both experimentally and theoretically about the behavior of anisotropic layered superconductors. Theoretically, such superconductors can be described either by a Ginzburg-Landau theory with an anisotropic κ[21] or as an array of Josephson-coupled layers[22] (which can be reduced in some limits to an anisotropic Ginzburg-Landau description). Consistent with our findings for $Y_1Ba_2Cu_3O_{7-x}$, this class of superconductors is known to possess anisotropic critical fields with $H_{c1}^{\perp}$ much larger than $H_{c1}^{\parallel}$ and differences in magnetization hysteresis loops and inferred critical-current densities. Though we have not studied the upper critical fields in our $Y_1Ba_2Cu_3O_{7-x}$ crystals, they can be expected to behave like those in other anisotropic layered superconductors, in which case $H_{c2}^{\parallel}$ is much larger than $H_{c2}^{\perp}$. Such behavior in $Y_1Ba_2Cu_3O_{7-x}$ would explain some disparate aspects of the early data on this material. In particular, measurements of the resistive transitions in high magnetic fields have indicated drastic broadening of the transition as field is applied.[2,23] In a ceramic composite of $Y_1Ba_2Cu_3O_{7-x}$, some grains oriented with their layers perpendicular to the field would possess modest critical fields. Other grains with their layers oriented parallel to the field would have enormous critical fields. The resulting resistive transition, as field is applied, would broaden in a manner consistent with the early observations. Pinning between weakly Josephson-coupled layers would be very weak resulting in small depinning critical currents perpendicular to the layers. The critical currents so far observed for ceramic materials have been in all cases small. To our knowledge the $\simeq 3\times10^6$-A/cm^2 values for critical current density in the direction of the Cu-O planes in our crystals at 4.5 K are the largest values yet seen in the $Y_1Ba_2Cu_3O_{7-x}$ materials. In general, pinning in perfect crystals is not expected to be strong, and so it is reasonable to expect that still higher critical current densities can be achieved. Indeed, recent results with epitaxial films,[24] with the epitaxy such that the large supercurrents flow along the direction of the Cu-O planes, have demonstrated larger high-temperature values of critical current density than ours, although the drop off with increasing field is more rapid.

In summary, our measurements on single crystals of $Y_1Ba_2Cu_3O_{7-x}$ demonstrate conclusively that its superconductivity is strongly anisotropic. At low temperatures in fields out to 40 kG, critical currents along the direction of the Cu-O planes were observed to be in excess of 10^6 A/cm^2. The large supercurrent-carrying capability and the anisotropy will be important aspects of most application considerations.

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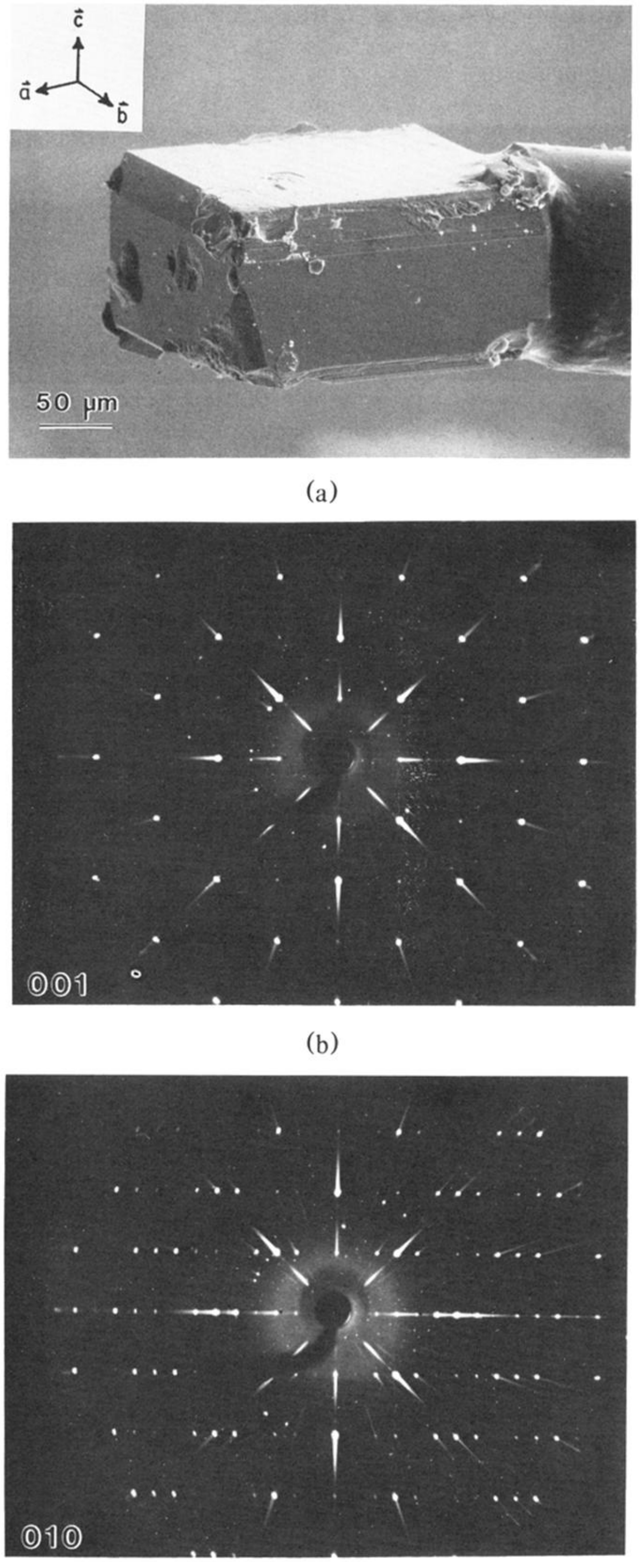

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