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CRITICAL CURRENT DENSITIES FOR THE HIGH TEMPERATURE CERAMIC SUPERCONDUCTORS $YBa_2Cu_3O_7$ and $Bi_2Sr_2Ca_2Cu_3O_{10+\delta}$

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SUPERCONDUCTORS $YBa_2Cu_3O_7$ AND $Bi_2Sr_2Ca_2Cu_3O_{10+\delta}$

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Abstract

A pulsed transport technique has been used to measure the zero field critical current densities of $YBa_2Cu_3O_7$ ceramic superconductors prepared under different sintering conditions. This low duty-cycle, pulsed technique, used on specially prepared samples with low resistance current contacts, allows one to determine the entire superconducting/normal phase boundary without the problems associated with sample heating. The results can be interpreted in terms of two different critical current densities. The intergrain critical current is low and is limited by the weak-links between the grains; the intrinsic intragrain critical current is greater than 10^4 A/cm^2 at 77K. Critical current values inferred from magnetic hysteresis measurements made on the same samples agree with the intrinsic intragrain critical currents obtained using the pulsed transport technique. In addition, the magnetization derived critical current density has been determined for the high T_c phase (n=3) of the $Bi_2Sr_2Ca_{n-1}Cu_nO_{2n+4+\delta}$ family at 77K.

Introduction

Since the discovery of the high T_c ceramic superconductors,[1,2] expectations of large scale applications such as motors, generators, levitated trains and advanced electronics, all removed from the specialized world of liquid helium technology, have been high. However, most applications of superconductivity require that the materials carry current densities on the order of 10^4 to 10^6 A/cm^2. To date, the highest value obtained by transport measurements on bulk samples of $YBa_2Cu_3O_7$ is 7400 A/cm^2 at 77K in melt-textured materials,[3] and in regular sintered samples typical values are a few hundred A/cm^2. This limitation, along with the natural brittleness and limited strength of the ceramic superconductors, has prevented the rapid exploitation of "high temperature" superconductivity.

While many workers report low transport critical currents on yttrium 1-2-3, other researchers have reported very high transport critical currents in epitaxial thin films.[4] Furthermore, high critical currents have been deduced from magnetization measurements on bulk samples, while the transport critical currents for these same samples are very low.[5] Thus, considerable uncertainty exists as to the inherent current carrying capacity of these materials. In this paper, we present evidence that the critical current intrinsic to $YBa_2Cu_3O_7$ is very high, and that the transport critical current in bulk sintered samples is limited by weak-links at the grain boundaries. These weak-links are due to Josephson junctions naturally occurring at the grain boundaries, or to anisotropy-limited conduction across misoriented adjacent grains.[6-8]

Experimental Technique

The critical currents were measured in zero applied magnetic field using a pulsed transport technique.[9] A further description of the technique will be published elsewhere. Briefly, a pulse generator is used to drive a programmable high-current source. The sample is wired in the usual four-probe fashion with a necked down section to achieve high current densities. The pulses of high current are generated at frequencies ranging from 2 to 10 Hz. The duty cycle, during which the pulse of current is on, is on the order of 0.1%. This value is adjusted as necessary so that the power dissipated in the sample (and at the current contacts) does not cause measurable sample heating. Thus, the pulse widths are typically 100 to 500 μsec. The pulse height, measured across a known series resistor, is monitored with an oscilloscope and is used to set the current, I, to a fixed value. The voltage pulse across the sample's voltage leads is sent through a differential amplifier and then measured with a box-car signal averager gated to measure the sample voltage, V, over a portion of the pulse. The sample resistance, R=V/I, is measured as the sample temperature is slowly varied.

This technique allows a quantitative determination of the sample resistance as a function of temperature which agrees with that obtained using conventional low-current DC techniques. The advantage of this technique over conventional high-current DC methods is that the entire superconducting transition can be studied without an increasingly resistive sample heating up. That is, a fraction of the sample going normal does not drive the entire sample normal because very little heat has a chance to flow during the short duration of the pulse. Applied to the superconducting ceramics, this means that when the intergranular weak-links go normal, the superconductivity of the individual grains can still be studied.

Sample Preparation

Samples were prepared from Y_2O_3 (99.99%), $BaCO_3$ (99.997%), Bi_2O_3 (99.9998%), $CaCO_3$ (99.9995%), CuO (99.999%), and $SrCO_3$ (99.99%), all used as obtained from Aesar. The $YBa_2Cu_3O_7$ samples were calcined at 925°C and then ground to a fine powder (with these processes repeated as necessary to obtain at least 95% of the theoretical weight loss). The powder was pressed into pellets at pressures ranging from 3 to 15 kbar. In the presence of flowing O_2, the pellets were sintered for several hours and annealed at 525°C for a few hours. The sintering conditions were varied to produce samples which were over-, normally-, and under-sintered (at temperatures of 990°C, 930°C, and 930°C, respectively). For the latter two types of sample, the sintering times and oxygen partial pressures were adjusted to achieve different sample hardness. The samples have densities of 65%, 73%, and 90% of the theoretical density of $YBa_2Cu_3O_7$ for the under-, normally-, and over-sintered samples, respectively (after correcting the over-sintered sample for the presence of 30% of the Y_2BaCuO_5 phase). The

hardness of these samples can be qualitatively described, respectively, as: somewhat soft (easily scratched with a hand tool), very hard (can be shaped with a file), and extremely hard (must be shaped with a grinding stone).

Low resistance (50-100 mΩ) contacts for the critical current measurements were made with silver paint (Dupont 4922 or 4929) which was baked onto the samples at 850°C in flowing O_2 for two hours.[10] The samples were then re-annealed at 525°C as before.

The $Bi_2Sr_2Ca_{n-1}Cu_nO_{2n+4+\delta}$ samples were calcined at 860°C (repeated as necessary to obtain the expected weight loss), then pressed into pellets, and sintered. The sintering was a multi-step process which is described elsewhere.[11] The samples were prepared to be of nominal molar composition Bi:Sr:Ca:Cu equal to 4:3:3:6. Silver contacts were then applied as described above. Depending on the exact processing used, some samples contained mostly the n=2 phase (T_c = 80K), while others contained mostly the n=3 phase (T_c=110K).[11]

Each sample was mounted to an anodized aluminum substrate using G.E. 7031 varnish. A groove was then machined down the center of the sample, using a diamond coated cutting wheel, so as to leave a small bridge approximately 1 mm^2 in cross-section connecting the ends of the two halves. All of the current densities reported here are calculated as the applied current divided by the cross-sectional area of this bridge. No correction is made for the fact that the samples are less than 100% dense.

Results and Discussion

The superconducting transition for a typical under-sintered sample of $YBa_2Cu_3O_7$ is illustrated in Fig. 1. Note that as the current density increases, a "foot" or "tail", as it is usually called, develops. As discussed in the previous section, the resistance measured by this technique is a quantitatively accurate measure of the total sample resistance. Thus, even for the highest current densities shown in the figure, most of the sample is still superconducting. The growth of the foot can be attributed to more and more of the weak-links in the sample going normal. These current density levels have very little effect on the main part of the transition near 90K. This will be discussed in more detail below.

Fig. 2 contrasts the superconducting transitions of over-sintered and under-sintered samples of $YBa_2Cu_3O_7$.

There is an unmistakable difference in the degree to which a foot develops in the over-sintered sample compared to the under-sintered sample. The weak-links in the over-sintered sample are apparently less "weak" or less numerous than in the under-sintered sample.

In Fig. 3, a magnified view of the superconducting transition is illustrated for the over-sintered sample of Fig. 2, except that larger and smaller current densities are also shown. The data for the lowest current density shown are found to be the same as that measured with a conventional low-current DC technique. The transitions for the normally-sintered sample of $YBa_2Cu_3O_7$ at various current densities are plotted in Fig. 4. This data should be compared to that of the under- and over-sintered samples of Figs. 1-3.

At a given current density J_c, the intersection of the resistive foot with the temperature axis (that is, the R=0 point) gives the critical current density at that temperature. This value of J_c is the same that one would obtain at that temperature using a conven-
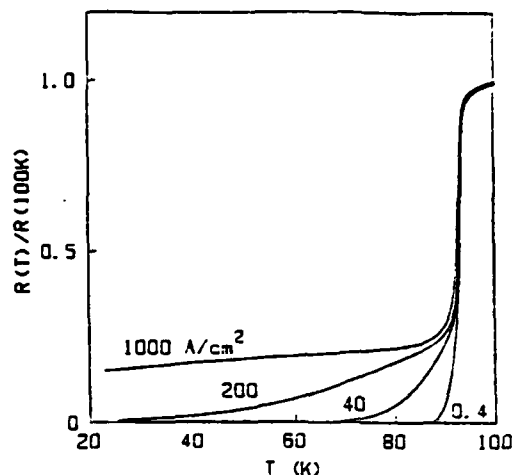

Figure 1. The superconducting transition of an under-sintered sample of $YBa_2Cu_3O_7$ at various current densities. The sample resistance at 100K is 40 mΩ.
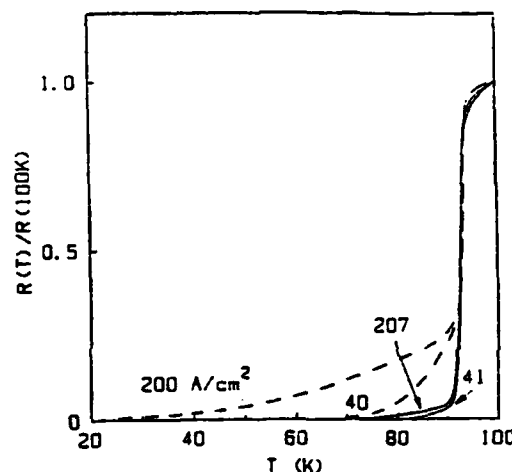

Figure 2. A comparison of the superconducting transitions for an over-sintered sample of $YBa_2Cu_3O_7$ (solid lines), and for an under-sintered sample (dashed lines). Two current densities, approximately 40 and 200 A/cm^2, are shown for each sample.
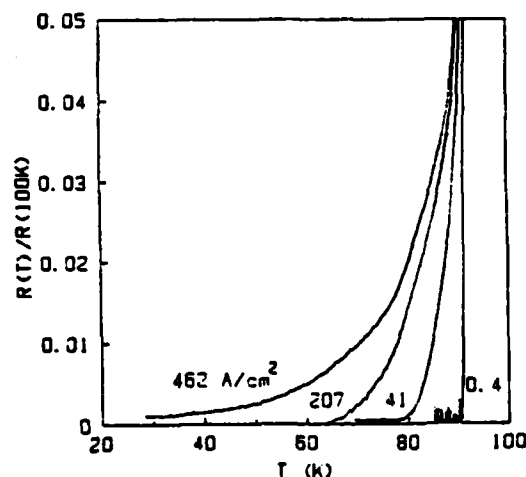

Figure 3. A magnified view of the superconducting transition for the same over-sintered sample illustrated in Fig. 2. The sample resistance at 100K is 11 mΩ.
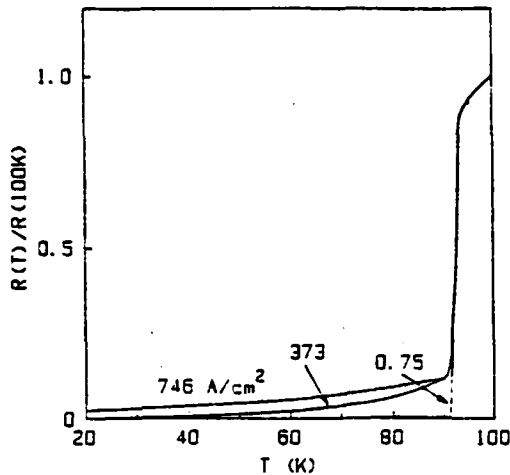
Figure 4. The superconducting transition of a normally-sintered sample of $YBa_2Cu_3O_7$ at various current densities. The sample resistance at 100K is 6mΩ.

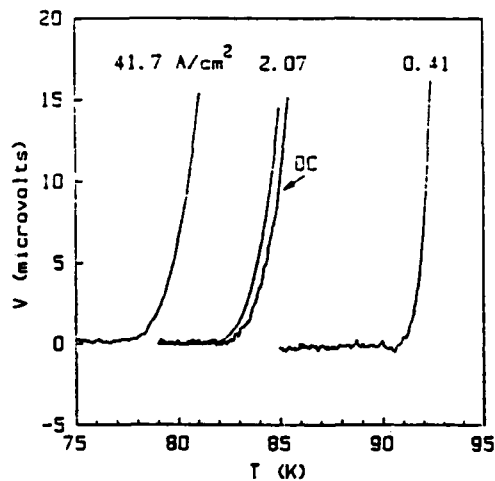**Figure 5.** A highly magnified view of the superconducting transition of an over-sintered sample of $YBa_2Cu_3O_7$ for three different current densities. The curve marked "DC" was measured with direct current, while all of the others were measured with pulsed current.
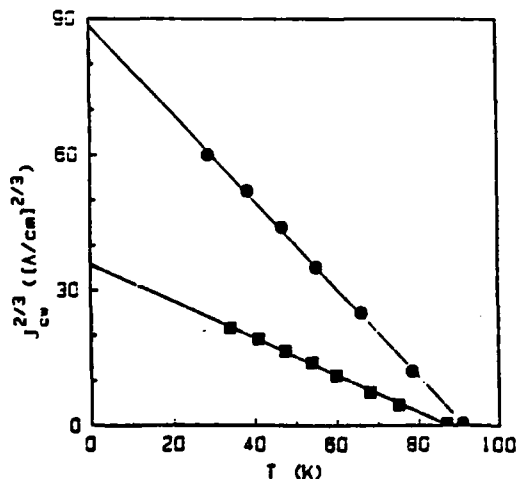

Figure 6. The weak-link critical current density to the two thirds power, $J_{cw}^{2/3}$, versus absolute temperature for over-sintered (circles) and under-sintered (squares) samples of $YBa_2Cu_3O_7$.

tional DC technique that measures current versus voltage at a fixed temperature. That this is in fact the case is clearly illustrated in Fig. 5, which shows a highly magnified view of the start of the resistive transition for the over-sintered sample for three different current densities. For the intermediate current density shown, the DC-determined resistive transition is also illustrated. There is clear agreement between the pulsed and DC data to within 0.5K.

Using this pulsed technique to measure the weak-link (R=0) critical current, J_{cw} ("w" for weak-link), we are able to determine the dependence of J_c on temperature. The results are illustrated in Fig. 6 for the over-sintered and under-sintered samples of $YBa_2Cu_3O_7$. An electric field criterion of 3 μV/cm was used in determining J_{cw} from data such as that in Fig. 5. The data can be fit rather well when plotted as $J_{cw}^{2/3}$ versus temperature. Note that the weak-link critical currents of the over-sintered sample are much greater than those of the under-sintered sample.
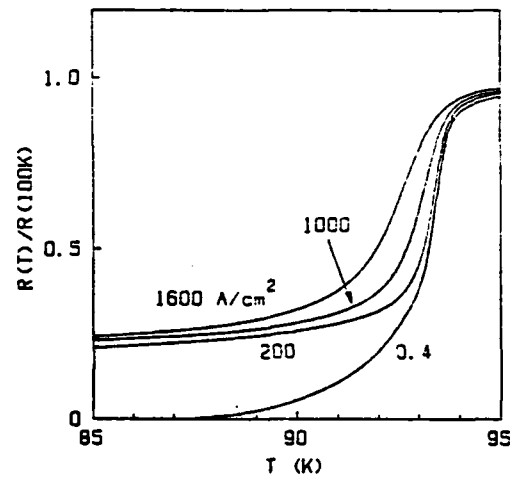

Figure 7. The main superconducting transition of an under-sintered sample of $YBa_2Cu_3O_7$ at various current densities. The temperature scale has been greatly expanded to show the shift in the transition midpoint.
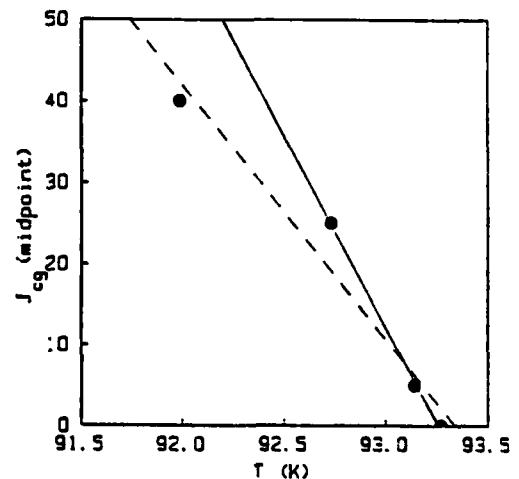

Figure 8. The intrinsic critical current density, J_{cg}, of the individual grains, versus absolute temperature for an under-sintered sample of $YBa_2Cu_3O_7$. Two different linear extrapolations give J_{cg}(77K) values of 2×10^4 A/cm^2 (dashed line) and 3×10^4 A/cm^2 (solid line).

In Fig. 7, the main superconducting transition is shown for the under-sintered sample. Note that as the current density increases, the resistance of the foot saturates. This represents the amount of current needed to drive all of the intergranular weak-links normal. Then as the current density increases further, the main drop in resistance of the bulk of the sample also moves to lower temperatures, as expected. This shift is caused by exceeding the intrinsic intragranular critical current, J_{cg} ("g" for grain), at this temperature. The data of Fig. 7 allows one to determine the intrinsic critical current versus temperature. The result for the same under-sintered sample that was represented in Fig. 7 is illustrated in Fig. 8, where J_{cg}, as determined from the transition midpoint, is plotted on a greatly expanded temperature scale. With the limited amount of data shown, the extrapolation to lower temperature is not definitive. However, two extreme fits are illustrated in the figure which allow an approximate extrapolation to 77K. This extrapolation yields a value of $(2-3) \times 10^4$ A/cm^2 for the intrinsic critical current density at 77K for this under-sintered sample of $YBa_2Cu_3O_7$.

Magnetization hysteresis measurements at 77K were made on these same $YBa_2Cu_3O_7$ samples, from which the intragranular critical current can be deduced according to the critical state model of Bean.[12] Examination by scanning electron microscope reveals approximate grain sizes of 17, 25 and 19 μm for the under-, normally, and over-sintered samples, respectively. Using these numbers gives magnetization J_{cg} values at zero magnetic field of 2×10^4, 3×10^4, and 3×10^4 A/cm^2, respectively, which are in excellent agreement with the values obtained from the pulsed transport measurements.

For the bismuth samples with mostly the $n \approx 2$ ($T_c \approx 80K$) phase, the magnetic hysteresis was too small at 77K to get reliable numbers for the critical current. For the samples with mostly $n=3$ ($T_c=110K$) phase, the magnetic hysteresis at 77K was comparable to that measured for the $YBa_2Cu_3O_7$. For an effective grain size of 20 μm, the critical current would be 5×10^4 A/cm^2. Detailed morphological studies and pulsed transport J_c measurements on the bismuth samples will be reported later.

Conclusion

In conclusion, we have presented evidence to show that the bulk transport critical current in sintered $YBa_2Cu_3O_7$ superconducting ceramics is limited by intergranular weak links. However, the intrinsic intragrain critical currents are quite high. Furthermore, the values obtained for bulk sintered samples by this pulsed transport method are consistent with those values inferred from magnetization hysteresis measurements on bulk samples, as well as with transport critical currents obtained for high quality epitaxial thin films.

Acknowledgments

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