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Direct measurements of the effects of inhomogeneities on the normal-state transport properties of $YBa_2Cu_3O_{7-x}$ thin films

A. D. Kent, I. Maggio-Aprile, Ph. Niedermann, and Ø. Fischer
Département de Physique de la Matière Condensée, Université de Genève, 24 quai Ernest Ansermet, CH-1211 Genève 4, Switzerland
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We have used a scanning tunneling microscope to measure both the topography and potential distribution in a current-carrying polycrystalline $YBa_2Cu_3O_{7-x}$ thin film. We find steps in the potential indicative of insulating inhomogeneities in the material which occur at boundaries between clusters of grains. These results provide the first direct correlation between the microstructure and the normal-state transport properties in these materials. The implications of these results for models used to explain the nature of superconductivity in polycrystalline high-temperature superconductors are discussed.

A number of the properties of high-temperature superconductors have been ascribed to granular superconductivity. For example, the results of measurements of the critical current,[1] the magnetization (and related relaxation phenomena),[2] the rf surface impedance,[3] and the resistive transition[4] in polycrystalline thin films and ceramics are interpreted as evidence for a weakly coupled granular material. In the superconducting state, direct measurement of the critical current across single grain boundaries has provided microscopic evidence for weakly coupled superconducting grains.[1] These results suggest that superconducting grains Josephson couple across insulating barriers in the material. In this Rapid Communication, we present the first direct microscopic evidence for such insulating inhomogeneities and are able to determine their position in a polycrystalline $YBa_2Cu_3O_{7-x}$ thin film. Our results provide a natural way of understanding the high resistivity and disorder effects in polycrystalline material.

We have used a scanning tunneling microscope (STM) to measure both the topography and potential distribution in a current-carrying polycrystalline Y-Ba-Cu-O thin film. The STM is operated in air at room temperature. We use a simple STM design in which it is possible to position a tip and sample with the aid of an optical microscope. The calibration and operation of this STM have been described in detail elsewhere.[5] The maximum scan area is large (15 μm $\times$ 5.5 μm). Because the surfaces we measure are quite rough, it is important to have sharp tunneling tips. We have used a combination of dc and ac electrochemically etched tungsten tips which have a radius of 1000–2000 Å from measurements in a scanning electron microscope (SEM). With these tips we find that it is possible to obtain reproducible topographic images at a voltage of 1 V and a tunneling current of 1 nA. Previous studies have demonstrated a good correspondence between STM and SEM images on thin films of Y-Ba-Cu-O.[6] We are thus confident that the STM images the real surface topography with some rounding of sharp features due to the finite tip radius.

The thin films used were prepared in a standard way by evaporation of the metal elements Y, Ba, and Cu in an oxygen atmosphere and subsequent annealing at high temperature in oxygen to produce the 1:2:3 phase.[7] The substrate used is Ca-stabilized ZrO_2. The films are stoichiometric and polycrystalline.[8] For STM and transport measurements the films were scribed with a diamond tip (to avoid disturbing the surface or the properties of the films with photolithographic patterning) in a strip geometry (1 mm width) and gold contacts (1000 Å thick) were evaporated to form Ohmic contacts.

For this study we have chosen nonideal superconducting thin films which clearly exhibit effects due to disorder or inhomogeneities. We have been able to make STM measurements on a number of such thin films and here we present results obtained on a typical disordered polycrystalline thin film. The resistive transition of this film is shown in Fig. 1. The onset temperature is 90 K and zero resistance occurs at 30 K. This behavior is similar to that seen in classic granular superconductors[9] as well as the results of other groups on Y-Ba-Cu-O films prepared on nonideal substrates.[10] The film resistance is 100 Ω/□ (thickness ~5000 Å, $\rho \sim 5$ mΩ cm) at room temperature

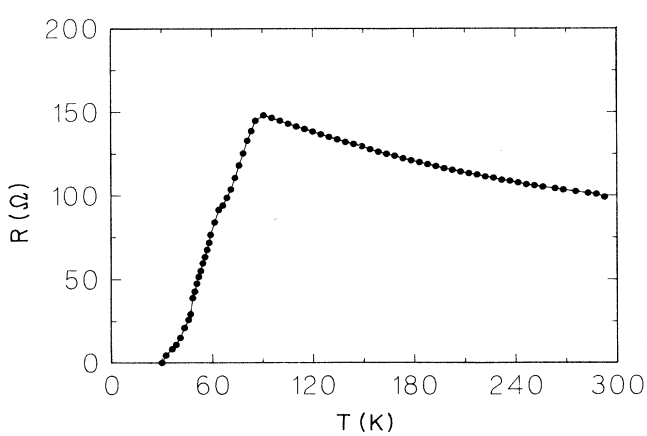

FIG. 1. Resistive superconducting transition of a disordered polycrystalline Y-Ba-Cu-O thin film (resistance per square vs temperature).

which ensures measurable potential changes with our STM. Direct calculation of the electron mean free path from this resistivity yields an unrealistically small value (smaller than the lattice constant) which also suggests that large-scale disorder plays an important role in this material. The surface roughness of the film is of the order of 2000 Å. The average grain diameter, 1 μm, is larger than the film thickness so that transport in this film is of a two-dimensional nature and we expect potential drops only in the plane of the film. We also note that the criteria for obtaining a sharp resistive superconductor transition in a two-dimensional granular thin film is much more severe than in three dimensions because of the difficulty of percolation in two dimensions. We thus expect a comparable ceramic material of the same resistivity to have a considerably sharper transition which is indeed the case.[4]

We have used a technique of scanning tunneling potentiometry developed recently by Kirtley, Washburn, and Brady[11] with some modifications to suit the measurement of Y-Ba-Cu-O thin films. This method differs from the original work of Muralt and Pohl[12] who were the first to use an STM as a fine-scale potentiometer. We apply a dc potential across a thin film as shown in the inset of Fig. 2 and a bias voltage V_b is introduced relative to ground at a point under the tip by means of a bridge circuit. The tip is held at virtual ground by a current-sensitive preamplifier. Topographic measurements are made in the usual way by maintaining a constant current and approximately constant tunneling voltage. The tunneling voltage will change slightly as the tip is moved because of the applied potential difference across the film, but this has a negligible effect on the actual tip height above the surface.[11] To measure V_s, the sample potential at the position of the tip, the STM feedback is suspended and the tunneling I-V_b characteristics are measured (Fig. 2). The intercept of this curve with the $I=0$ axis determines the sample potential. To facilitate scanning, the waveforms shown in the inset of Fig. 2 are used. Measurements of the current are made at bias voltages both greater and less than the sample potential while the STM feedback is suspended. Linear interpolation is then used to deduce the sample potential. Typical bias voltages used are +5 and −5 meV and these measurements take from 10 to 500 msec depending on the averaging necessary. Our method differs from that of Ref. 11 in that we use a large voltage to control the tip to sample distance (1 V), which we find necessary to obtain reproducible topography data, while we use relatively low voltages for determining the sample potential.

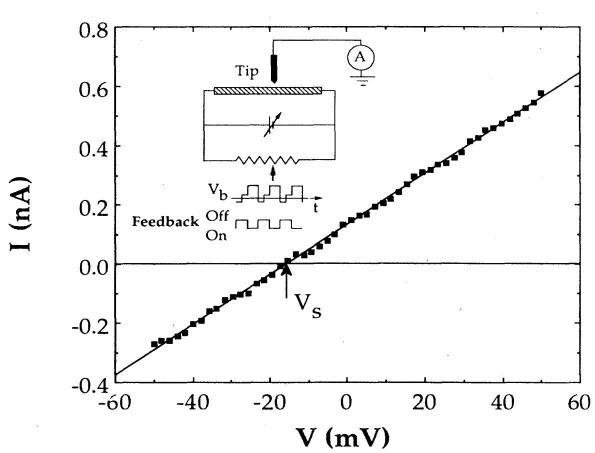

FIG. 2. Typical I-V_b curve showing the linear current-voltage characteristics and the determination of the sample potential from this measurement. The inset of this figure shows the circuit and waveforms used for scanning tunneling potentiometry.

In Fig. 3 we show a gray scale image of topography and potentiometry obtained simultaneously with an applied electric field of 8 V/cm and a current density of 1.6 $\times 10^3$A/cm^2. This is an image of a 5×5 μm area and consists of 400×50 pixels of topographic information and 100×50 pixels of potentiometric information. The gray scales for topography cover a range of 2000 Å from black (low) to white (high). The scales for potentiometric data are 15 mV from black (low potential) to white (high potential). The long thin grains we observe are typical of the grain structure seen in an SEM. Current is flowing from left to right in this figure and we resolve an average

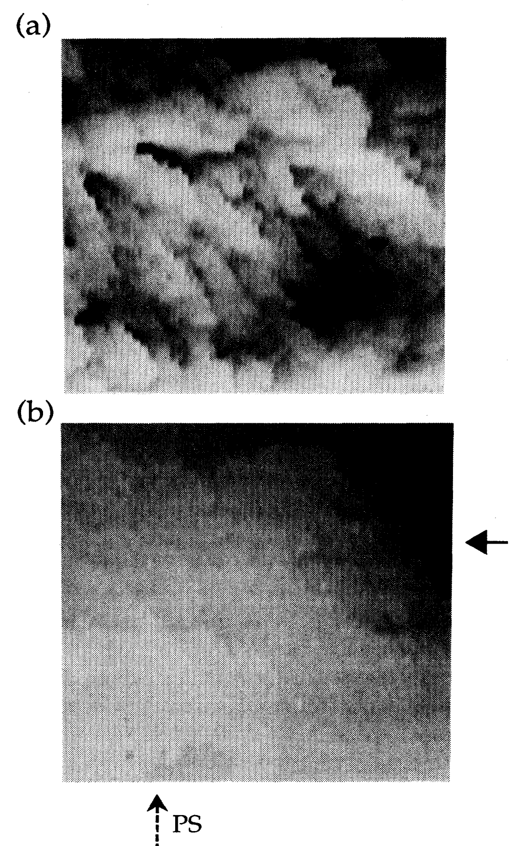

FIG. 3. (a) Topographic and (b) potentiometric gray scale images of a Y-Ba-Cu-O thin film acquired simultaneously with an applied field of 8 V/cm (applied from left to right in these figures). The images are of a 5 μm×5 μm area. For topography the gray scale is 2000 Å from black (low) to white (high) and for potentiometry the scale is 15 mV from black (low potential) to white (high potential).

potential drop across this 5 μm length of 5.1 mV. This is to be compared with the 4 mV drop expected for a uniform potential drop in this film.

The most significant results, however, are the discrete steps in the potential which we observe in Fig. 3(b). In this figure areas of nearly constant levels of gray shading represent approximately equipotential regions and the abrupt changes in gray shading indicate that there are steps in the local potential. These steps imply that resistance in this film is associated with spatially well-defined boundaries in the material. This is exactly the situation envisioned by Landauer in 1957 for transport in a disordered metal.[13] Landauer considered the one-dimensional case of transport in a metal with a current incident normal to infinite plane reflecting barriers characterized by a reflection coefficient r. This can be considered a model for grain boundaries or stacking faults in a metal. In contrast with the conventional Boltzmann picture in which a constant gradient in the potential is assumed, a voltage drop was predicted in the immediate vicinity of the barriers as a direct consequence of the transport current. The resistivity of the material was found to be proportional to the density of obstacles and $r/(1-r)$. Our potentiometric measurements support such a view of transport in this material. The large macroscopic resistivity we measure must thus be considered a consequence of barriers in the material (with $r \rightarrow 1$) and not of properties intrinsic to the material (such as the mean free path in the Boltzmann picture). Since our material is two dimensional and has a distribution of barrier heights, one must view the potential steps as a consequence of barriers which are critical to the percolation of the current across the sample (i.e., barriers which cannot be bypassed by lower resistance barriers or paths in the material).

The terraces in the potential image [Fig. 3(b)] can be considered indicative of a distribution of insulating barriers in the material. The exact source of these barriers is not clear; they may be due to insulating impurity phases (including oxygen-deficient Y-Ba-Cu-O) or intrinsic properties of certain structural features in this material. We do find that a number of steps in potential in Fig. 3(b) correlate well with topographic features which we identify as grain boundaries [Fig. 3(a)]. We thus see direct evidence for the general speculation that insulating grain boundaries are a source of the disorder in Y-Ba-Cu-O material. However, we also see in Fig. 3(b) that drops in potential occur quite nonuniformly. There are clusters of grains which have roughly the same potential (within the 0.5-mV resolution of the measurement). In addition, we observe regions of the material in which the potential does not decrease monotonically. For example, in the lower part of Fig. 3(b) (shown with the dashed arrow labeled PS) we see a step in potential of opposite sign to applied potential drop. This also shows that large variations exist in the effective resistance of barriers in the material.

In Fig. 4 we show in detail a large step in the potential we have observed in the upper right-hand region of Fig. 3(b) (shown with solid arrow). This shows the abrupt change in potential due to insulating boundaries in the material. We have scanned over the same region three times, with positive applied voltage, no applied voltage,

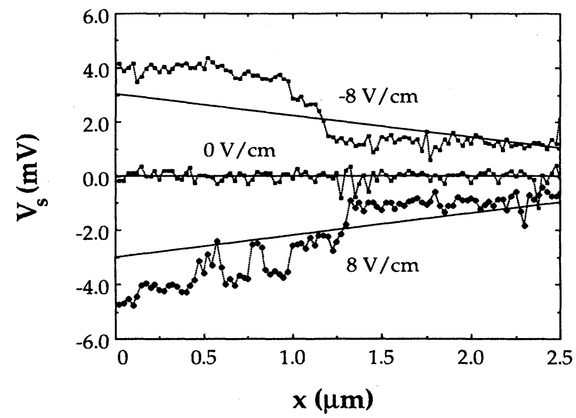

FIG. 4. Single line scans across the step indicated with a solid arrow in Fig. 3(b) along the direction of the applied field x. The curves from top to bottom are applied fields of -8, 0, 8 V/cm respectively. The top and bottom curves have been offset from zero for clarity. The uniform potential distribution expected for these applied fields are also shown (solid straight lines).

and negative applied voltage. We thus see that the measured potential drop is directly related to the applied voltage and the potential drop in this area is associated mainly with two discrete steps.

We now consider the implications of these results on models of granular superconductivity. Our results clearly show that insulating boundaries exist between more metallic grains or clusters of grains. If these grains are assumed to be superconducting, this shows that the material can be modeled as a superconductor-insulator-type granular composite. We do note, however, that the length scale of inhomogeneities which dominate the normal-state transport and presumably the superconducting properties occur on a scale larger than the grain size. The properties of these insulating boundaries are also extremely variable, and this variability must be taken into account in any realistic model of the disorder. To what extent the insulating boundaries we see can account for the superconducting properties is still unclear. For example, the broad resistive transition we observe in Fig. 1 would normally be ascribed to granular superconductivity with fully superconducting grains with the bulk transition temperature, which would have to Josephson couple to produce zero resistance in the film. It is the ratio of the Josephson coupling energy (which is inversely proportional to the grain boundary resistance) to the thermal energy which determines the transition temperature of such a system.[14] However, the magnitude of the grain boundary resistance is not large enough to produce the suppression of the superconducting transition temperature we observe in Fig. 1. Using the largest potential drops we have measured, and assuming that the average current-density flows through these boundaries, the specific resistance of a grain boundary is given by $R_s = \Delta V/j$, where j is the average current-density in the film. Taking $\Delta V = 2$ mV we find $R_s = 1.3 \times 10^{-6}$ $\Omega\,\mathrm{cm}^2$. If we take the film thickness times the grain diameter as an estimate of the contact area between grains we find an intergrain resistance of 250 Ω. (This is, of course, the intergrain resistance at room temperature, but given the weak temperature dependence of the resistance seen in Fig. 1 we do not expect a large change in this value with temperature.) Not surprisingly, this is the same order of magnitude as the resistance per square of the film. This resistance would not produce a significant depression in the transition temperature of the film since two superconducting grains separated by this resistive barrier would Josephson couple extremely close to the transition temperature of the individual grains.[14] To account for the suppression in the superconducting transition temperature one would then have to postulate a severe reduction in the coupling between grains perhaps due to a reduction in the superconducting order parameter at the grain surface. Of course, it is also possible that there is a depression in the grain transition temperature or a combination of these phenomena which produce the superconducting properties seen in these films.

In conclusion, we have shown that the technique of scanning tunneling potentiometry can be applied to understanding the microscopic nature of electron transport in Y-Ba-Cu-O thin films. Our results show that there is a distribution of insulating inhomogeneities in the material which are responsible for the large normal-state resistivity. We are currently extending these studies to low-temperature to examine in detail the nature of the resistive transition in polycrystalline thin films.

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[1]J. Manhart, P. Chaudhari, D. Dimos, C. C. Tsuei, and T. R. McGuire, Phys. Rev. Lett. **61**, 2476 (1988), and references therein.

[2]K. A. Müller, M. Takashige, and J. G. Bednorz, Phys. Rev. Lett. **58**, 1143 (1987).

[3]T. Hylton, A. Kapitulnik, M. R. Beasley, J. P. Carini, L. Dieaski, and G. Grüner, Appl. Phys. Lett. **53**, 1343 (1988).

[4]M. A. Dubson, S. T. Herbert, J. J. Calabrese, D. C. Harris, B. R. Patton, and J. C. Garland, Phys. Rev. Lett. **60**, 1061 (1988).

[5]R. Emch, Ph. Niedermann, and P. Descouts, J. Microsc. (to be published).

[6]Ph. Niedermann and Ø. Fischer, J. Microsc. (to be published).

[7]B. Oh, M. Naito, S. Arnason, P. Rosenthal, R. Barton, M. R. Beasley, T. H. Geballe, R. H. Hammond, and A. Kapitulnik, Appl. Phys. Lett. **51**, 852 (1987).

[8]J-.M. Triscone, L. Antognazza, M. G. Karkut, and Ø. Fischer, Physica C **153-155**, 786 (1988).

[9]See, for example, *Inhomogeneous Superconductors—1979,* edited by D. U. Gubser, T. L. Francavilla, R. R. Leibowitz, and S. A. Wolf, AIP Conference Proceedings No. 58 (American Institute of Physics, New York, 1980).

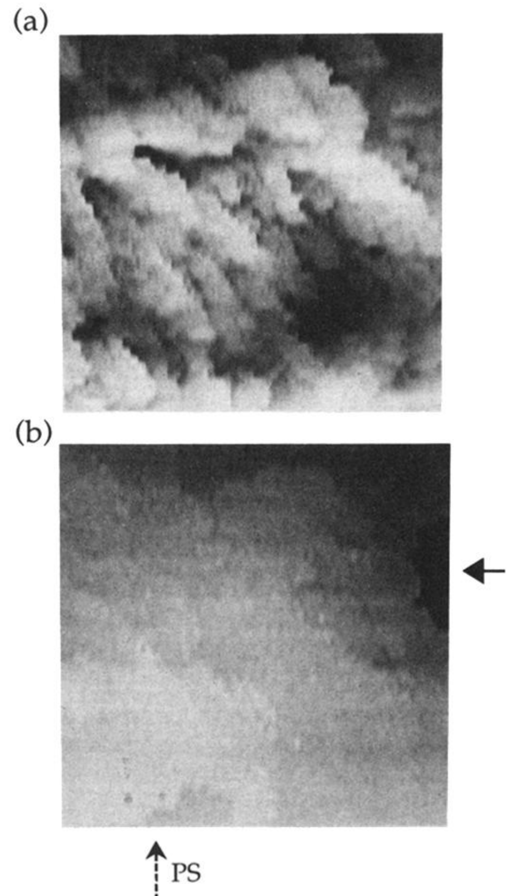
[10]K. Char, A. D. Kent, A. Kapitulnik, M. R. Beasley, and T. H. Geballe, Appl. Phys. Lett. **51**, 1370 (1987).

[11]J. R. Kirtley, S. Washburn, and M. J. Brady, Phys. Rev. Lett. **60**, 1546 (1988); IBM J. Res. Dev. **32**, 414 (1988).

[12]P. Muralt and D. W. Pohl, Appl. Phys. Lett. **48**, 514 (1986).

[13]R. Landauer, IBM J. Res. Dev. **1**, 223 (1957); Z. Phys. B **21**, 247 (1975).

[14]O. Entin-Wohlman, A. Kapitulnik, and Y. Shapira, Phys. Rev. B **24**, 6464 (1981).



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