Low-temperature resistivity of $YBa_2Cu_3O_{6+x}$ single crystals in the normal state

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A scan of the superconductor–nonsuperconductor transformation in single crystals of $YBa_2Cu_3O_{6+x}$ ($x \approx 0.37$) is done in two alternative ways, namely, by applying a magnetic field and by reducing the hole concentration through oxygen rearrangement. The in-plane normal-state resistivity ρ_{ab} obtained in the two cases is quite similar; its temperature dependence can be fitted by a logarithmic law in a temperature range of almost two decades. However, an alternative representation of the temperature dependence of $\sigma_{ab}=1/\rho_{ab}$ by a power law, typical for a 3D material near a metal–insulator transition, is also plausible. The vertical conductivity $\sigma_c=1/\rho_c$ followed a power law, and neither $\sigma_c(T)$, nor $\rho_c(T)$ could be fitted by log *T*. It follows from the ρ_c measurements that the transformation at $T=0$ is split into two transitions: superconductor–normal-metal and normal-metal–insulator. In our samples, they are separated in oxygen content by $\Delta x \approx 0.025$. © *1997 American Institute of Physics.* [S0021-3640(97)00711-1]

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In this paper we intend to apply the scaling theory of localization[1] to the underdoped system $YBa_2Cu_3O_{6+x}$. The theory[1] allows one to classify the temperature dependence of the conductivity in the close vicinity of the metal–insulator transition in a 3D material. There is a critical region near the transition in which the conductivity $\sigma(T)$ follows a power law

$$\sigma=\alpha+\beta T^m. \tag{1}$$

When the main inelastic processes in the critical region are controlled by the electron–electron interaction, the exponent $m=1/3$ (Refs. 2 and 3). The constant α in the relation (1) is negative, $\alpha<0$, and the critical region there is bounded from below by a crossover temperature T^* on the insulating side of the transition. Below T^*, the conductivity falls off exponentially:[4,5]

$$\sigma \propto \exp[-(T_0/T)^n], \quad n=1,\ 1/2,\ \text{or}\ 1/4. \tag{2}$$

The crossover temperature T^* and the constant α both become zero at the transition point, so that $\sigma(T)$ at this point is proportional to $T^{1/3}$ (Refs. 2 and 3):

$$\sigma = \beta T^{1/3}. \tag{3}$$

This relation can be used for detecting the transition point.

A low-temperature crossover line exists in the critical region of the transition on the metallic side too. The conductivity here is described by dimensionless equation[6]

$$s^{3/2} = s^{1/2} + t^{1/2}, \quad s = \sigma(T)/\sigma(0), \quad t = T/T^*. \tag{4}$$

The function $s(t)$ goes over to the power laws (1) in the opposite temperature limits, with $\alpha = \sigma(0)$ and $m = 1/2$ at low temperatures, when $t \ll 1$, and with $\alpha = \frac{2}{3}\sigma(0)$ and $m = 1/3$ when $t \gg 1$. It follows from Eq. (4) that at the crossover temperature, when $t = 1$, the conductivity is $\sigma(T^*) = 1.75\, \sigma(0)$.

According to the theory,[1] a normal-metal–insulator transition does not exist in 2D materials: any film is expected to become insulating at $T = 0$. With decreasing temperature, the localization starts with the so called quantum corrections to the classical conductivity σ_0:

$$\sigma = \sigma_0 + \Delta\sigma = \sigma_0 + \gamma_\sigma \log T, \quad \Delta\sigma \ll \sigma_0. \tag{5}$$

The relation $\Delta\sigma < \sigma_0$ cannot be violated because the conductivity $\sigma(T)$ is always positive. When σ_0 and $\Delta\sigma$ become comparable, the weak localization turns into strong localization and the logarithmic behavior (5) gives way to the exponential behavior (2): at low enough temperature $\sigma(T)$ should fall off exponentially.

When the metal is superconducting the pattern of the transition to the insulating state changes. In 2D the superconductor–insulator transition has been observed experimentally.[7] In 3D it is not clear whether such a transition can take place as a single transition or whether it would occur through a normal-metal intermediate state. In order to study the low-temperature behavior of a superconductor, one can bring it to the transition, suppress the superconductivity by a magnetic field H, and then investigate the transition and its vicinity with the field held constant. It had been assumed that a material with supressed superconductivity would behave at finite temperatures as an ordinary metal. However, since 1980 there have been repeated experimental indications that fpr superconducting materials there is an intermediate region in the vicinity of the transition in which the normal resistivity varies logarithmically with temperature:[8]

$$\rho(T) = \rho_0 + \Delta\rho = \rho_0 - \gamma_\rho \log T. \tag{6}$$

The temperature dependence (6) has been found in granular aluminum[8] and granular niobium nitride films,[9] in percolating lead films,[10] and in $Nd_{2-x}Ce_xCuO_{4-y}$ ceramics.[11] In all these cases the resistance changes severalfold over the range of the logarithmic temperature dependence, the logarithmic term in (6) becoming the leading one at low temperature:

$$\Delta\rho \gg \rho_0. \tag{7}$$

Hence relation (6) cannot be converted into (5) despite the formal resemblance between them.

Interest in this problem has been renewed after the publications by Ando, Boebinger, *et al.*,[12,13] which revealed the $\log T$ term in the resistivity of underdoped $La_{2-x}Sr_xCuO_4$ in pulsed magnetic fields of 60 T. This interest has several aspects.

(i) As the volume of experimental data is rather poor, one cannot be confident and must check whether the $\log T$ term really exists — it is not simple nor even always possible to distinguish between $\log T$ and a power-law dependence (1).

(ii) What are the specific properties of those materials for which this term appears? If these should turn out to be exclusively high-T_c superconductors[11–14] it would point to a specific role of strong correlations in electron systems; on the other hand, it may turn out that it is granularity which is of primary importance.[8–11,14]

Motivated by these goals, we present below the measurements of the temperature dependence of the in-plane ρ_{ab} and vertical ρ_c resistance of the single crystals $YBa_2Cu_3O_{6+x}$. By decreasing the doping level in high-T_c superconductor systems, one can suppress the superconducting transition temperature T_c and bring the system to the boundary of the superconducting region. In the YBaCuO system this can be done by decreasing the oxygen content or, in a limited range, by oxygen rearrangement in the planes of CuO chains.[15,16]

Single crystals of $YBa_2Cu_3O_{6+x}$ were grown by the flux method in alumina crucibles.[17] Oxygenated at 500 °C in flowing oxygen, they had a T_c of about 90–92 K and a fairly narrow resistive transition $\Delta T_c < 1$ K. To bring the samples to the boundary of the superconducting region, the oxygen content was reduced by high-temperature (770–820 °C) annealing in air with subsequent quenching in liquid nitrogen.[16,17] To rearrange the chain-layer oxygen subsystem, the $YBa_2Cu_3O_{6+x}$ crystal was heated to 120–140 °C and quenched in liquid nitrogen. This procedure reduces the mean length of the Cu–O chains; hence, the hole doping of CuO_2 planes decreases.[18,19] The equilibrium state, with a larger hole density, can be restored simply by room-temperature aging. By dosing the aging time, one can also obtain intermediate states. Thus the quenching–aging procedure allows one to vary gradually the charge carrier density and to tune the sample state through the boundary of the superconducting region.

Special care was taken to measure reliably the separate resistivity components. The in-plane resistivity was measured on thin (20–40 μm thick) plate-like crystals by the four-probe method with current contacts covering two opposite lateral surfaces of the crystal.[17] The contacts were painted on with silver paste and were fixed by annealing. To measure the vertical resistivity, circular current electrodes were painted on the opposite sides of the plate, with potential probes in the middle of the circles. The resistivity was measured by the standard low-frequency (23 Hz) lock-in technique in the temperature range 0.37–300 K, the measuring current being low enough to avoid any sign of sample overheating even at the lowest temperature.

Below we present the temperature dependence of the in-plane resistivity obtained for the ''aged'' and ''quenched'' states of one of the $YBa_2Cu_3O_{6+x}$ ($x \approx 0.37$) crystals. For both states the resistivity passed through a minimum near 50 K. The ratio r of the resistance at room temperature to that at minimum was ≈ 3. (In terms of classical metal physics this means that the crystal is not perfect: crystals for which $r \approx 10$ do exist.) In the quenched state, no signs of the superconducting transition were observed on the $\rho(T)$

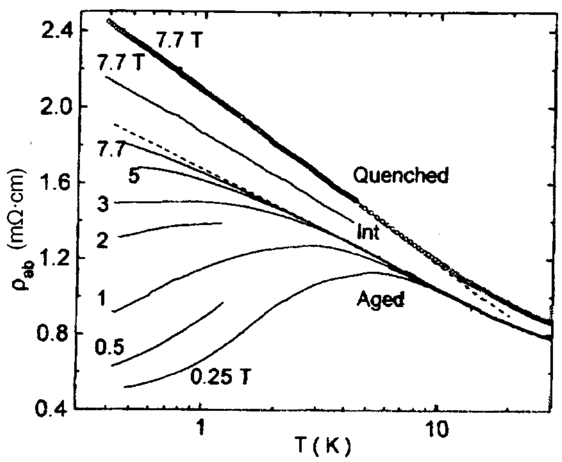

FIG. 1. In-plane resistivity versus log T for a YBaCuO single crystal with a fixed oxygen content but with different oxygen arrangements (quenched, intermediate, and aged states). Only the aged state is superconducting, and the set of curves demonstrates how a field $\mathbf{H}\|c$ destroys the superconductivity. The dashed lines are an extrapolation of the linear dependence $\rho_{ab}(\log T)$. Experimental points are plotted only on one curve.

curve down to the lowest temperature. In the aged state, the resistivity growth at low temperatures was interrupted by the superconducting transition. Owing to the low $T_c < 10$ K, the superconducting transition could be suppressed almost completely by the available magnetic field $\mathbf{H}\|c$.

Attempts to fit the $\rho_{ab}(T)$ data by an exponential law (2) were unsuccessful. On the contrary, we succeeded in fitting the data by the logarithmic law (5); see Fig. 1. The quenched and the intermediate states, which both lack superconductivity, exhibited a resistivity which increased logarithmically with decreasing T over almost two decades of temperature. The magnetoresistance of the quenched state was below 1%; thus the perfect fit demonstrated in Fig. 1 obtains both with and without a magnetic field. It can be seen that with increasing magnetic field the $\rho_{ab}(T)$ curves for the aged state make a step-by-step approach to a straight line. Apparently the deviations from the logarithmic law (5) indicate only that the highest applied field 7.7 T was not strong enough. Thus the representation of the data given in Fig. 1 agrees with that of Refs. 11–14.

However, this is not the only possible interpretation. Assuming that our sample is a 3D material, we can analyze the data with the help of Eqs. (1) and (4). According to Fig. 2, the data for the quenched state of the sample, replotted as σ versus $T^{1/3}$, approach a straight line at large T and satisfy Eq. (4) with the parameter values $\sigma(0) = 0.23$ MS/cm and $T^* = 0.37$ K. The values for the intermediate state are $\sigma(0) = 0.32$ MS/cm and $T^* = 1.25$ K. Thus this approach is self-consistent: the aging of the sample increases the hole density and thereby leads to an increase of the conductance $\sigma(0)$ and crossover temperature T^*.

Therefore, at this stage we cannot choose between the log T and T^m representations, i.e., between representations (5) and (1), (4). We have done experiments on a crystal with $r \approx 10$, too, but were left with the same uncertainty. However, in any case the supercon-

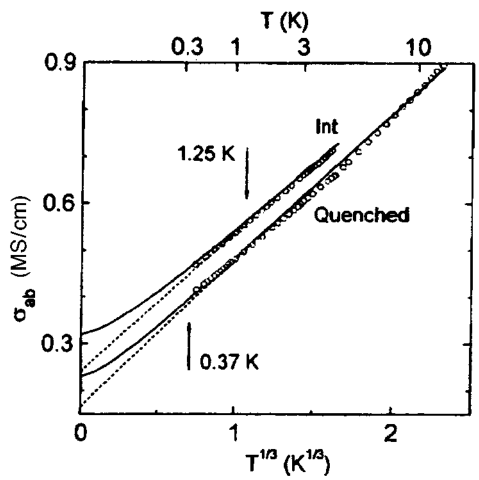

FIG. 2. The data for quenched and intermediate states from Fig. 1 replotted as σ_{ab} vs $T^{1/3}$. Solid lines – fits by Eq. (3) with the T^* values indicated by arrows, dashed lines – asymptotes in the $t \gg 1$ region.

ducting state does not give way directly to an insulator: representation (5) would indicate that it converts into some specific strongly correlated metallic state, while representation (1) would point to a normal-metal state. The conclusion that the transformation in YBaCuO consists of two stages: into normal metal first and into insulator after further decrease of the hole density, was made previously[20] on the basis of an extrapolation of the transport data from high temperatures (from above the resistance minimum). Here the extrapolation edge is far lower — only 0.4 K.

The transport properties of YBaCuO crystals near the boundary of the superconducting region are highly anisotropic, the ratio ρ_c/ρ_{ab} exceeding 10^3 (Ref. 21). The crystals can be regarded as a stack of weakly bound conducting CuO_2 planes. This brings some uncertainty to the question of whether the in-plane transport should be considered to be of a 2D or of 3D type. At the same time the vertical transport is certainly 3D, and its temperature dependence is of special interest. We have measured several crystals and present below examples of typical behavior.

Figure 3 shows the ρ_c data for two crystals annealed in air at 800 °C: $c1$ and $c2$, each in two states, quenched (curves $c1_{\mathrm{q}}$ and $c2_{\mathrm{q}}$) and aged ($c1_{\mathrm{a}}$ and $c2_{\mathrm{a}}$). They certainly do not follow log T, but perfectly fit the $T^{1/3}$ representation (1) with α of different signs; see inset. Hence, these aged and quenched states should be placed on different sides of the metal–insulator transition. All the data presented were obtained with a magnetic field of 7.7 T, but the magnetoresistance was small and did not affect the representation.

In the left-hand part of Fig. 3 we present in addition the curve $c1_{\mathrm{q}}'$ obtained for the crystal $c1$ annealed at 780 °C and quenched; the curve is fit by Eq. (4) with $\sigma_0 = 1.5\alpha = 0.18$ S/cm. The aged state of the crystal with this oxygen content reveals symptoms of superconductivity, such as the onset of a kink and positive magnetoresistance at lower temperatures. Hence, these aged and quenched states should be placed on

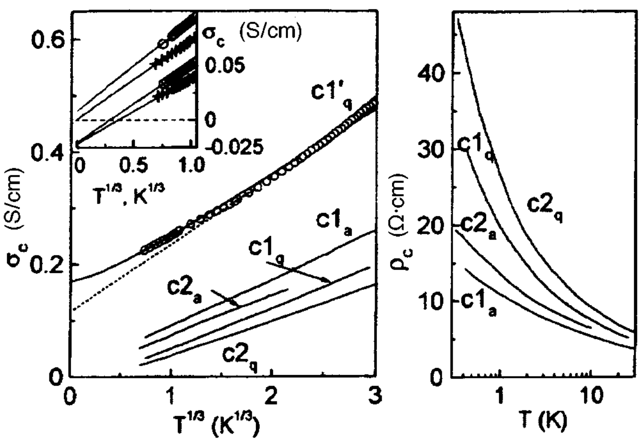

FIG. 3. Vertical resistivity data for two crystals, $c1$ and $c2$, plotted as σ_c versus $T^{1/3}$ (left) and as ρ_c versus $\log T$ (right). The experimental points have been removed from several of the curves. The inset shows an enlarged part of the main plot.

different sides of the superconductor–normal-metal transition on the phase diagram in Figs. 5 and 7 of Ref. 16. According to these diagrams, in the 800 °C range of annealing temperatures a 20° change results in a difference of $\Delta x \approx 0.025$ in the oxygen content and in a difference of $\Delta n/n_c \approx 0.07$ in the hole concentration n normalized to the critical value n_c. Although the precise positions of the two transitions may depend on the degree of disorder in the crystals, the numbers obtained can be regarded as estimates of the distance between the superconductor–normal-metal and the metal–insulator transitions along the abscissa of the phase diagram.

In conclusion, the low-temperature $\rho_c(T)$ curves of $YBa_2Cu_3O_{6+x}$ ($x \approx 0.37$) single crystals follow a scaling temperature dependence in the vicinity of the metal–insulator transition and permit one to specify the transition point. The difference in the oxygen concentration x between this point and that of the normal-metal–superconductor transition is approximately $\Delta x \approx 0.025$. It remains still unclear whether the representation of the in-plane resistivity $\rho_{ab}(T)$ in the region between these transitions on a $\log T$ scale is meaningful or whether the description by the functions (1) and (4) is more adequate.

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