

Out-of-plane conductivity of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$

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Pressure measurements on successively heat-treated $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ single crystals suggest that the out-of-plane resistivity (ρ_c) is diffusive even if $d\rho_c/dT$ is positive in high-quality samples. $d\rho_c/dT > 0$ comes from the temperature dependence of the in-plane lifetime of the particles which tunnel to the neighboring planes and $d\rho_c/dT < 0$ is due to phonon-assisted hopping when disorder is introduced between the CuO layers.

The copper-oxide-based high-temperature superconductors have highly anisotropic properties in both the superconducting and normal states. The reason for this anisotropy lies in the crystal structure: The highly conductive CuO planes (ab crystallographic planes) are separated by low-conductivity layers (in the c crystallographic direction). This two dimensionality (2D) results in different types of transport properties for the different directions for most high- T_c oxides: metallic transport in the ab plane and nonmetallic along the c axis.¹ It seems that the only exception is $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$, where in high-quality samples even the c -axis resistivity (ρ_c) has a metallic temperature dependence²⁻⁴ ($d\rho_c/dT > 0$). It is known that on reducing the oxygen content of this compound, an activated temperature dependence of ρ_c shows up, but the precise reason for this behavior is not known.

In this Brief Report we report the results of a study of ρ_c of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ single crystals under hydrostatic pressure. We have measured the same single crystal with high oxygen stoichiometry ($\delta \sim 0.07$, $T_c = 90$ K) and low oxygen content ($\delta \sim 0.5$, $T_c = 51$ K). We argue that $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ fits into the general picture where the ab plane resistivity is metallic and the c -axis resistivity is diffusive, because the estimated mean free path in the c direction is less than or equal to the c -lattice parameter. Reducing the oxygen content of the sample, we increase disorder, which makes the transverse tunneling and, in consequence, ρ_c activated. In systems such as $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$, even in the "perfect crystal" the interplane transfer is already thermally activated and is presumably phonon-assisted hopping.⁵

In this work we have used two grain-growth single crystals: one for the pressure study at high and low oxygen content and one for measuring the effect of low oxygen deficiency. The typical sample dimensions were $0.5 \times 0.5 \times 0.2$ mm³. Crystal growth and characterization are described in Ref. 6. The main characteristics are the following. On a crystal size of 0.2 cm³ (grown for neutron-diffraction studies), the mosaic spread was about 0.3°. On smaller crystals, suitable for transport studies, optical microscopy of the ab surface of the crystals shows

twin boundaries and homogeneous voids (up to 8% of the surface area) running in the c direction. High-resolution electron-microscopy studies on several crystals did not reveal stacking defects in the c direction, making unlikely the mixing of ab and c -axis conduction channels. Voids facilitate oxygen diffusion in the crystal, and one can obtain a better oxygen distribution than in flux-grown samples. Contact resistances of $< 1 \Omega$ were obtained by silver epoxy. The contact arrangement for a four-probe resistivity measurement is given in the inset of Fig. 1, where, for the sake of comparison, we also give the ab -plane resistivity. ρ_c has been measured in a special Montgomery-type configuration. This contact arrangement, with extended current pads, is more close to a direct c -axis measurement than the Montgomery method, which is based on point contacts. However, because the current pads do not entirely cover the ab face of the crystal, some reduction of the current density results below the voltage pads. This reduction is more important for thin samples and low anisotropies. On lowering the temperature, the anisotropy increases because of the different slopes $\rho_c(T)$ and $\rho_{ab}(T)$. As a result, the current density below the voltage pads will increase. This effect will always increase the measured resistance on lowering T .

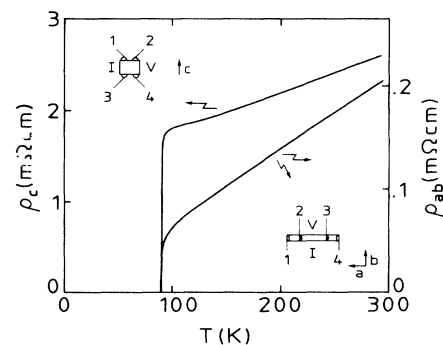


FIG. 1. Resistivity-temperature curves for current flow parallel (ρ_{ab}) and perpendicular (ρ_c) to the CuO_2 layers of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$. Sketch of contact geometry is also shown.

Thus, in samples with metallic ρ_c , one can observe an upturn at low T because of the nonideal contact configuration. But, of course, if one observes a metallic behavior, the true behavior will be even more metallic. Thus the ρ_c -vs- T profiles with a slight upturn have to be seen with some caution. However, the very pronounced negative slope of the $T_c=51$ K sample will not be affected by these small corrections. Pressure measurements have been performed in a clamped system described in Ref. 7.

Figure 1 shows the ab -plane and c -axis resistivities. Measurements on several crystals showed that for a well-oxygenated crystal ρ_{ab} is typically 200–300 $\mu\Omega$ cm at room temperature, while ρ_c varies between 2.5 and 5 m Ω cm. ρ_{ab} has a very low intercept (“residual resistivity” ρ_0). For the c -axis resistivity, ρ_c^0 , the extrapolated value at $T=0$, is usually in the m Ω cm range.

Figure 2 shows ρ_c versus temperature for a highly oxygenated crystal at several pressures. At 1 bar, $\rho_c=2.5$ m Ω cm at 300 K and $\rho_c^0=1.2$ m Ω cm. Under pressure ρ_c decreases with an initial rate $\sim 1.5\%/kbar$ at room temperature, this rate is strongly temperature dependent, and just above the superconducting transition temperature (T_c), it increases to 3.5%/kbar. (ρ_{ab} decreases with an initial rate $\sim 1.0\%/kbar$ in the whole temperature range.) T_c increases with a rate $dT_c/dP=0.055$ K/kbar. As shown in the inset to Fig. 2, the temperature dependence of $d \ln \rho_c/dP$ is such that the extrapolated residual resistivity ρ_c^0 falls by more than 30% under pressure, while the slope $d\rho_c/dT$ hardly changes. This surprising feature provided the initial motivation for us to consider models in which the c -axis motion occurs via incoherent hopping even though $d\rho_c/dT > 0$. It also turns out that the perpendicular mean free path is always too small for a standard band picture to apply. Namely, in a simple band picture, ρ_c is given by

$$\rho_c = \frac{1}{e^2 n(E_F) v_{\perp}^2} \left\{ \frac{1}{\tau_e} + \frac{1}{\tau_i(T)} \right\}, \quad (1)$$

where $n(E_F)$ is the electronic density of states, v_{\perp}^2 is the

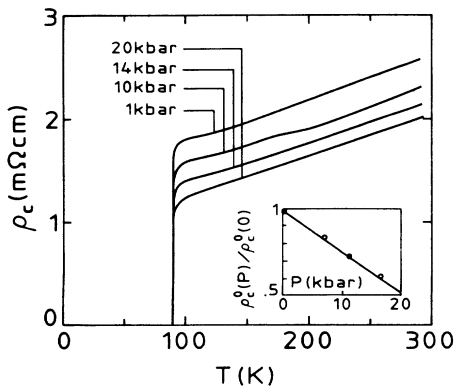


FIG. 2. Temperature dependence of ρ_c for several pressures. The inset shows the pressure dependence of the residual resistivity ρ_c^0 .

mean-square Fermi velocity in the c direction, τ_e^{-1} is the elastic-scattering rate from impurities or disorder, and $\tau_i(T)^{-1}$ is the inelastic-scattering rate from phonons or other excitation processes. In a tight-binding picture, $(v_{\perp}^2)^{1/2} = \sqrt{2} t_{\perp} c/h$, where t_{\perp} is the transverse overlap integral and c the lattice parameter. The mean free path perpendicular to the planes is $l_{\perp} = v_{\perp} (\tau_e^{-1} + \tau_i^{-1})^{-1}$. In order to estimate l_{\perp} from the data in Fig. 1 by using Eq. (1), one needs to know v_{\perp} and $n(E_F)$ or actually, at least, the ratio of v_{\perp}/v_{\parallel} . From band-structure calculations,⁸ $n(E_F) = 76$ states/(unit cell)/Rydberg, $\sqrt{v_{\perp}^2} = 0.7 \times 10^7$ cm/sec, and the ratio $v_{\perp}/v_{\parallel} = 0.39$. In a tight-binding picture, this value of v_{\perp} corresponds to a perpendicular transfer integral $t_{\perp} = 0.026$ eV or 320 K. Substituting the above values into Eq. (1) leads to $l_{\perp} = 2.8$ Å for $\rho_c = 1$ m Ω cm. Generally, one would expect the condition $l_{\perp} \leq c$ ($c = 11.7$ Å) to represent the limits of validity of the band picture. Alternatively, the ratio of the measured slopes $[(d\rho_c/dT)/(d\rho_{ab}/dT)]$ can be used to estimate v_{\perp}/v_{\parallel} with the assumption that τ_i is isotropic. The measured ratio of 6.4 (Fig. 1) leads to the same values of v_{\perp}/v_{\parallel} and l_{\perp} . Thus, if the estimated value of t_{\perp} is correct, l_{\perp} is only of order $c/10$ near room temperature; the inelastic- and elastic-scattering lengths are approximately equal, but nevertheless experimentally $d\rho_c/dT > 0$.

A similar problem occurred previously for quasi-one-dimensional organic conductors where the resistivity is a few m Ω cm along the chains and several Ω cm between the chains at room temperature. Even though the (in this case inelastic) mean free path perpendicular to the chains is very short (as low as 0.005 lattice constants in some cases⁹), $d\rho_c/dT$ is still > 0 . Soda *et al.*¹⁰ have given a simple explanation for $d\rho_{\perp}/dT > 0$. Supposing coherent on-chain and incoherent interchain couplings, i.e., $t_{\perp} < h\tau_{\parallel}^{-1} < t_{\parallel}$ (τ_{\parallel}^{-1} and t_{\parallel} are the on-chain scattering rate and overlap integral, respectively), the transverse resistivity reads

$$\rho_{\perp} = [n(E_F) e^2 l^2 \tau_{\perp}^{-1}]^{-1}, \quad (2)$$

where $l^2 \tau_{\perp}^{-1} = D_{\perp}$ is the diffusion coefficient, l is the jumping distance, and τ_{\perp}^{-1} is the jumping frequency. τ_{\perp}^{-1} is given by

$$\tau_{\perp}^{-1} = (2/h) |t_{\perp}|^2 \tau_{\parallel} / h. \quad (3)$$

Inserting (3) into (2), it turns out that the transverse resistivity is

$$\rho_{\perp} \sim |t_{\perp}|^{-2} \tau_{\parallel}^{-1}, \quad (4)$$

and one can easily understand the linear temperature dependence and strong pressure dependence of ρ_c . This expression is exactly the same as the resistivity obtained in a band picture in the relaxation time approximation [Eq. (1)]. But unlike the band picture, it is still valid for arbitrary small values of τ_{\parallel} , i.e., of σ_{\parallel} , provided $l_{\perp} \gg a$ (l_{\parallel} is the on-chain mean free path, and a is the on-chain lattice spacing). However it only applied if the interplane tunneling matrix element couples states with the same energy. If the energy of the initial and final states is different or if, before getting to the final state the carrier

hops into intermediate states with mismatched energies, the interplane jumping process becomes phonon-assisted hopping with a hopping rate¹¹

$$\tau_{\perp}^{-1} = (\tau_{\perp}^{-1})_0 \exp(-\Delta E/k_B T)^{\alpha}, \quad (5)$$

where $(\tau_{\perp}^{-1})_0$ is the spatial tunneling factor and ΔE is the energy difference between the states. The exponent α depends on the dimensionality of the hopping.

A slightly different interpretation of our data makes use of ideas introduced in the field of weak localization. For an isotropic disordered system,¹² the condition $l_i > l_e$ is sufficient for localization to set in and to reduce the conductivity below the band value. If the data in Figs. 1 and 2 are interpreted within a band picture, then for c -axis motion $l_i \approx l_e$ at room temperature in the fully oxygenated samples. As the temperature is lowered, $l_i > l_e$ and there could be localization effects in the conductivity which depend on the ratio l_i/l_e .

Calculations for anisotropic systems¹³ show that localization should set in for both directions simultaneously, which seems to imply that localization is not relevant for the c -axis resistivity of, for example, $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$. However, the present case is slightly unusual in that l_e appears to be very anisotropic (Fig. 1). (Comparing our data with work on high-purity untwinned crystals,⁴ we estimate that l_e for the a direction should be at least 100 Å and for this direction $l_i < l_e$ down to ~ 10 K.) Indeed, Koshelev¹⁴ has pointed out that in high- T_c oxides, planar defects would only change the particle momentum in the c direction and could therefore give localization perpendicular to the planes while the in-plane conductivity remained metallic. Furthermore, the approach of Kaveh and Mott¹⁵ emphasizes the connection between localization and the asymptotic power-law behavior of the wave functions. It seems plausible that in the present case these could decay more quickly in the c direction and cause anisotropic localization. In this model one could account for the T dependence of $d \ln \rho_c / dT$ by considering different behavior of l_i and l_e under pressure.

In general, the strong T dependence of $d \ln \rho_c / dP$ may be an indication that localization effects (either according to Weger's theory or from a weak-localization viewpoint) are becoming more important at low temperatures.

Figure 3 demonstrates the gradual switch on of the activated behavior of ρ_c as we change the heat treatment of the same single crystal: (a) heat treated in 1 atm O_2 at 414°C, $d\rho/dT$ is positive; (b) heat treated in 1 atm O_2 at 454°C and quenched to room temperature, activated behavior appears below ~ 150 K; and (c) heat treated in 0.1 atm O_2 partial pressure at 454°C and quenched to room temperature, the activated behavior is present in a larger temperature range. During these successive heat treatments, the room-temperature value of ρ_c increased, and T_c started to shift down slightly for the last step. The high sensitivity of ρ_c to heat treatment has been already shown by us^{3,16} and recently confirmed by Ito *et al.*¹

As oxygen is removed, the residual resistivity ρ_c^0 increases from 1 to ~ 3 mΩ cm; thus l_{\perp}^e becomes shorter, while l_i , which corresponds to the high-temperature slope $d\rho_c/dT$, remains essentially constant. The nonmetallic

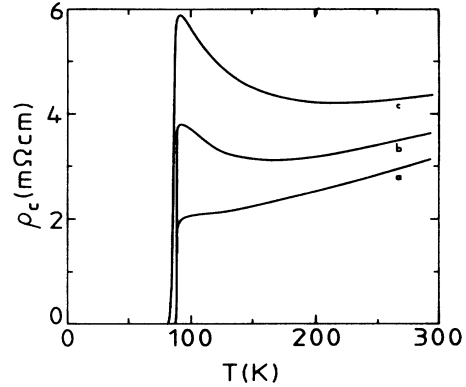


FIG. 3. ρ_c vs temperature at ambient pressure after successive heat treatments: (a) heat treated in 1 atm O_2 at 414°C, (b) heat treated in 1 atm O_2 at 454°C and quenched to room temperature, and (c) heat treated in 0.1 atm O_2 partial pressure at 454°C and quenched to room temperature.

regime extends to higher temperature as would be expected if weak localization associated with the crossover from $l_{\perp}^e < l_{\perp}^i$ to $l_{\perp}^e > l_{\perp}^i$ were occurring.

Further reduction of the oxygen partial pressure (0.01 atm at 454°C) increases ρ_c to 60 mΩ cm at 300 K, and it is activated down to the superconducting transition region ~ 51 K (Fig. 4).

In this case the nonmetallic behavior is probably associated with strong localization, that is, with phonon-assisted hopping between localized states described by Eq. (5). The phonon-assisted hopping may come from the slightly different Fermi level of the neighboring CuO planes or sandwiches, because of the difference in charge transfer from the charge reservoir (chains). This sometimes manifests itself in a cascade of superconducting transition temperatures in ρ_c , especially in flux-grown crystals. However, it is more likely that the disorder created in between the planes by oxygen depletion or disorder in the oxygen distribution caused by rapid quenching from high temperatures is at the origin of the phonon-assisted hopping in the c direction. This hopping process is quite complex in this complicated structure.

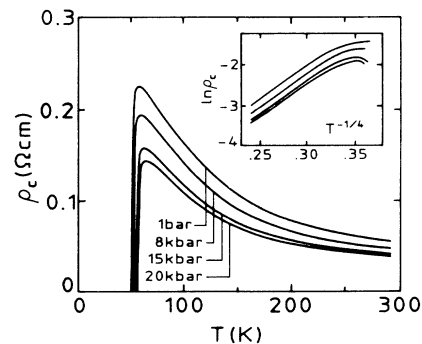


FIG. 4. ρ_c vs temperature of oxygen-depleted $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ ($\delta \sim 0.5$) at several pressures. The inset shows the same data on a $\ln \rho_c$ -vs- $T^{-1/4}$ plot.

For example, it is probably not a single-phonon-assisted hopping at these temperatures, and so one cannot expect a well-defined exponent α . Although there is no reason to expect $\alpha = \frac{1}{4}$ in such an anisotropic system, in the inset of Fig. 4 we have plotted $\ln\rho_c$ vs $T^{-1/4}$ just to illustrate another effect. If we measure ρ_c under pressure, the curves on the $\ln\rho_c$ -vs- $T^{-\alpha}$ plot are simply shifted downward for increasing pressure (independent of the choice of α). This means that the curves do not extrapolate at $T^{-\alpha}=0$ to the same value in contrast to band-gap semiconductors [e.g., K_3MoO_3 (Ref. 17)] or simple disordered systems such as polymers.¹⁸ We deal with the pressure dependence of the spatial interplane tunneling factor $(\tau_1^{-1})_0$ in Eq. (5). (Note that for this “low- T_c ” sample T_c shifts up at a rate of 0.35 K/kbar.)

We can mention that the phonon-assisted hopping and weak-localization models suggested above can give a hint for the temperature dependence of the resistivity anisotropy in the $T_c=90$ K sample (see Fig. 1). One possible explanation is that even in the present case there is some energy-level mismatch since t_\perp (~ 320 K) is small. As T is lowered, kT becomes of the order of the energy-level mismatch for some electronic states and there is a gradual changeover from Eq. (3) to Eq. (5). This might explain the changeover of the high-temperature positive slope of ρ_c into a negative one at low temperatures in some measurements.^{19,20} Alternatively, in the weak-localization picture, the anisotropy is T dependent simply because for the c direction $l_e < l_i$ and localization corrections are

significant, whereas in the ab plane $l_e \gg l_i$.

Most of our results can be explained by the holon-spinon tunneling model of Anderson and Zou,²¹ where ρ_c also depends on the interplane tunneling matrix element. However, it seems that this model fails to account for $d\rho_c/dT > 0$ of the highly oxygenated sample.

In conclusion, we have demonstrated that the out-of-plane resistivity of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ fits into the general picture of high-temperature superconducting oxides, where ρ_c is diffusive and the in-plane resistivity is coherent, although $d\rho_c/dT$ is positive in high-quality samples. By analogy with 1D conductors, $d\rho_c/dT > 0$ comes from the temperature dependence of the in-plane lifetime of the particle that controls the tunneling rate to the neighboring plane, and $d\rho_c/dT < 0$ is due to phonon-assisted hopping when disorder is introduced between the CuO layers. By varying the oxygen content and applying pressure, the c -axis resistivity can be varied from being metallic to what seems to be a type of phonon-assisted hopping between localized states. From a somewhat different viewpoint, there seems to be a region of weakly localized behavior where for the c direction the elastic mean free path is less than the inelastic one and the conductivity therefore starts to fall.

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