T^2 dependence of the resistivity in the Cu-O chains of $YBa_2Cu_3O_{6.9}$

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The temperature dependence of the electrical resistivity along the a and b axes of $YBa_2Cu_3O_{6.9}$ has been measured in high-purity fully detwinned single crystals. Below 300 K, $\rho_a(T)$ was found to be perfectly linear, while $\rho_b(T)$ revealed a distinct upward curvature. Viewing the b-axis conductivity as the sum of conductivities in the CuO_2 planes and along the Cu-O chains, a T^2 dependence for the chain resistivity is obtained. Such a dependence, also found in quasi-one-dimensional conductors, explains a number of hitherto ill-identified deviations from linearity reported recently.

Studies of electron behavior in high-T_c superconductors have concentrated mainly on the CuO_2 planes that are the fundamental building blocks of these oxides, where superconductivity is thought to originate. From early on, a linear temperature dependence of the electrical resistivity in the normal state has been considered a key characteristic property of the planes. Widely taken as generic and universal, a linear resistivity has been observed in most optimally doped compounds for a current parallel to the CuO_2 planes.[1] In $YBa_2Cu_3O_{7-\delta}$ (with δ close to 0), the CuO_2 planes are interspaced with Cu-O chains which lie along the b-axis of the orthorhombic crystal structure, parallel to the planes. The role of these chains in the electronic behavior both of the normal and superconducting states has attracted attention recently, for example, with reports of an associated Fermi surface[2] and an associated superconducting gap.[3] Moreover, recent studies show that the temperature dependence of the resistivity in the a-b plane of that compound is *not* linear. A distinct upturn in $\rho(T)$ has been observed both in powders[4] and in thin films[5]—a feature already apparent in earlier work on crystals.[6,7,9] Although the upturn has been attributed to the chains, to this day there is no detailed description of the separate conduction of planes and chains in $YBa_2Cu_3O_{7-\delta}$ (YBCO).

In this paper, we show that conduction in the Cu-O chains is very different to that of the CuO_2 planes: While the chain resistivity extrapolates to a high residual value at low temperatures and obeys a T^2 dependence up to room temperature, the planes are characterized by negligible residual resistivity and perfect linear dependence. Information of this kind could only be obtained by measuring the resistivity of a single crystal along the a and b axes separately. Given that in most as-grown crystals extensive (110)-type twinning occurs in the a-b plane, this usually requires artificially detwinned crystals. By using such crystals, Friedmann *et al.*[7] were the first to report the separate temperature dependence of ρ_a and ρ_b. Their two crystals were grown in yttria-stabilized zirconia (YSZ) crucibles. An anisotropy factor ρ_a/ρ_b=2.2±0.2 was obtained for 150< T <275 K. Both ρ_a and ρ_b were reported to be linear in temperature above the fluctuation regime. For one crystal, a slight upward curvature can be seen in both ρ_a and ρ_b above 240 K. For the other crystal, no curvature is evident. The authors did not attempt to explain these features. In addition, from a comparison between their detwinned crystals and twinned crystals of other groups, they suggested that twin boundaries significantly increase the planar resistivity. Soon after, Welp *et al.*[8] reported a similar study, based in this case on crystals grown in gold crucibles. The anisotopy factor ρ_a/ρ_b was found to be lower and sample dependent, ranging from 1.2 to 1.85. This dependence was attributed to a high sensitivity of the chain resistance to oxygen disorder. Both ρ_a and ρ_b were found to be linear in temperature, all the way from near T_c (≈130 K) up to 300 K. No deviations from linearity were detected. It is now known that growth in gold crucibles introduces up to several percent gold impurities on the Cu-O chains. This will increase the chain resistivity and hence reduce the anisotropy and mask any manifestation of intrinsic chain behavior. In this paper, we revisit the anisotropy of the in-plane resistivity of $YBa_2Cu_3O_{7-\delta}$ (with $\delta \approx$ 0.1), having used improved single crystals (larger, more fully detwinned and without gold impurities) and gone to higher temperature.

The crystals were grown by a self-flux method,[9] starting with powders of Y_2O_3 (99.9999%), $BaCO_3$ (99.999%), and CuO (99.9999%) mixed in a molar ratio Y:Ba:Cu of 1:18:45. YSZ crucibles were used, as they are known to contaminate YBCO crystals very weakly.[9] Crystals were oxygenated for 6 days at 500°C in flowing O_2 gas and quenched at room temperature. The oxygen content is expected to be 6.90< $7-\delta$ <6.92, based on existing oxygen diffusivity studies.[10] The oxygenated crystals were microtwinned almost uniformly over their entire surface. Those with the most rectangular shapes and without macroscopic defects were chosen for detwinning, which was achieved by applying a uniaxial pressure of approximately 50 MPa at 550 °C in air for 30 min or less. Detwinned crystals were then reoxygenated for 1 day at 500 °C in O_2. Electrical contacts were made with silver epoxy, annealed on the crystals at 500 °C in O_2 for 1 h, giving 40 μm diameter contacts with resistances of less than 0.1 Ω. The in-plane resistivity of detwinned crystals was measured at low frequency (16 Hz) using the Montgomery configuration,[11] i.e., with a contact on each of four corners of a rectangular a-b surface.

Two different runs were necessary to measure $R_a(T)$ and $R_b(T)$ from which were then calculated $\rho_a(T)$ and $\rho_b(T)$, knowing the sample dimensions l'_a, l'_b, l'_c and using the standard equations of Ref. 11, with the approximation $l_c/(l_a l_b)^{1/2} << 1$, where l_a, l_b, and l_c are the dimensions of an equivalent isotropic crystal. Because of the large ρ_c (of order 5 mΩ cm at room temperature[7]), this approximation was at the limit of its range of validity. To ensure the accuracy of the results, a parallel study was performed on crystals prepared in identical conditions and measured with the usual linear four-probe technique with uniform current distribution. All findings of both methods are in perfect agreement. The advantage of the Montgomery technique is that it gives a more accurate anisotropy factor and a more reliable determination of the chain resistivity, ρ_a and ρ_b being obtained from the same crystal. In this study, four detwinned crystals were investigated and the results on all four are closely consistent. Two were used for the Montgomery technique (labeled No. 1, with l'_a =0.95, l'_b=1.43, l'_c=0.10 mm, and No. 2, with l'_a=1.05, l'_b=0.61, l'_c=0.05 mm), and the other two served as double-checks using the linear four-probe technique. All crystals are characterized by a transition temperature of at least 93.4 and at most 93.7 K, with 10–90% widths of between 0.1 and 0.2 K. Crystal No. 1 was used to investigate the impact of the detwinning procedure, and the effect of twin boundaries on the resistivity. A measurement of the Montgomery resistances before and after detwinning revealed little impact: T_c neither shifted nor broadened. The extent of detwinning in crystal No. 1 was not perfect. Inspection by high-resolution polarized optical microscopy easily revealed the presence of about ten second-type domains with an average width of 1 μm. These extended through the thickness of the sample, giving a total volume fraction of misaligned domains of less than 1%. On the other hand, crystal No. 2 was perfectly detwinned, insofar as the microscope investigation revealed no twin boundaries whatsoever.

The in-plane resistivity of crystal No. 1 as a function of temperature is shown in Fig. 1, both before and after detwinning. Because a comparison of the absolute values is desired, special care went into establishing the correct geometric factors: The aspect ratio (length/width) was tuned so as to give an anisotropy factor of 1.0 in the twinned case, and then used in both cases. If one assumes an equal number of a- and b-oriented domains, then the "isotropic" resistivity of the twinned crystal would be $\rho_{tw} = (\rho_a+\rho_b)/2$ if the twin boundaries do not increase the planar resistivity. This is indeed what is obtained from the data of Fig. 1, within the experimental uncertainty of 20% (due to reinstallation of contacts at the corners after detwinning). At T=250 K, for example, ρ_{tw}=190 $\mu\Omega$ cm, while ρ_a=280, ρ_b=130, so that $(\rho_a+\rho_b)/2$=205 $\mu\Omega$ cm. We conclude that twin boundaries are *not* a significant scattering mechanism, contrary to what has been suggested.[7] We believe that variations in the oxygen annealing temperature and in impurity levels (not to mention the uncertainty in measuring absolute values on submillimeter crystals) are responsible for the sizable differences observed in the resistivity of

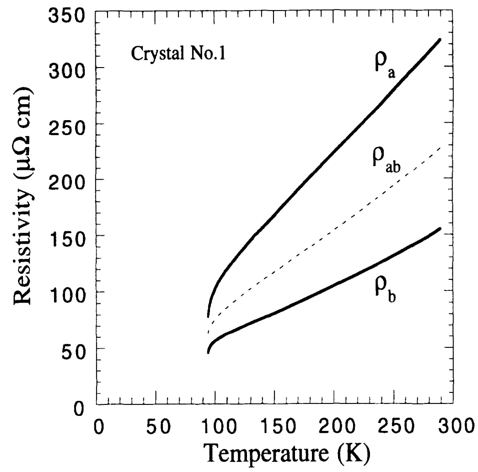

FIG. 1. Resistivity of crystal No. 1 as a function of temperature, for a current along the a axis (ρ_a) and the b axis (ρ_b), as obtained from the Montgomery technique. Note that ρ_a(T) is perfectly linear above 130 K, while a distinct upward curvature is observed for $\rho_b(T)$. The dashed curve is the resistivity ρ_{ab} of the same crystal prior to detwinning.

twinned and detwinned crystals coming from different groups. The anisotropy ratio is in agreement with the value of 2.2±0.2 previously found in the best samples:[7] ρ_a/ρ_b=2.15±0.05 at T=250 K.

What has not previously been recognized, however, is the qualitative difference in the dependence of $\rho_a(T)$ and $\rho_b(T)$. Above the superconducting fluctuation regime ($T_c < T <$130 K), ρ_a is found to be perfectly linear in temperature up to 300 K. On the other hand, ρ_b displays a smooth upward curvature. Such a nonlinearity has been detected before for $\rho_b(T)$ but, while less pronounced, it was also present in $\rho_a(T)$,[7] most likely due to residual twinning. Fully twinned crystals will exhibit the deviation from linearity, but with a smaller magnitude, as seen in Fig. 1 (dashed curve ρ_{ab}). In practice, it is easily visible only above 250 K, as seen on resistivity curves of previous reports.[6,9] In order to gain insight into the precise temperature dependence of the chain resistivity, we apply a simple model of parallel conduction channels to the b-axis conductivity, viewing it as a sum of separate conductivities in the CuO_2 planes and along the Cu-O chains. The chain resistivity $\rho_{chain}(T)$ is then given by $\rho_{chain} = \rho_a\rho_b/(\rho_a - \rho_b)$, where the plane resistivity is assumed isotropic with $\rho_{plane}=\rho_a$. The resistivity of the chains and the planes obtained within this model is shown in Fig. 2. The first thing to note is that they are of the same magnitude, as expected from an anisotropy ratio close to 2.0. The second, striking feature is the different temperature dependences: $\rho_{plane}(T)$ is linear; $\rho_{chain}(T)$ is quadratic. The T^2 dependence is made evident in Fig. 3 where a perfectly linear behavior as a function of T^2 is obtained in the range from 180 to 280 K, with a very slight downward curvature below that interval. Note that the same analysis performed on crystal No. 2 yields the same results. All our measurements on twinned and detwinned crystals of high purity can be consistently summarized by the following succinct

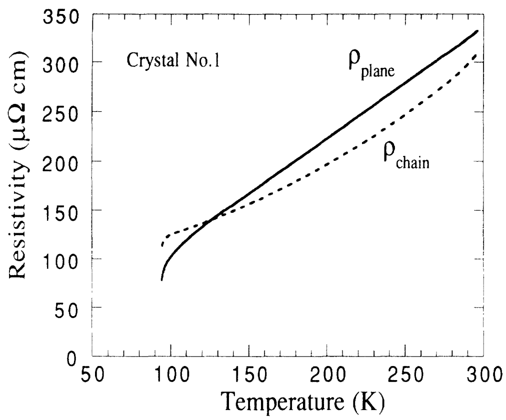

FIG. 2. Temperature dependence of the resistivity of Cu-O chains (ρ_{chain}, dashed curve) and of CuO_2 planes (ρ_{plane}, solid curve) using ρ_a and ρ_b data of Fig. 1, within a simple model of two parallel conduction channels for the b axis. ρ_a is taken to be the isotropic in-plane component and $\rho_{\text{chain}} = \rho_a\rho_b/(\rho_a - \rho_b)$.

expressions:

$$\rho_{\text{plane}} = T, \quad (1a)$$

$$\rho_{\text{chain}} = 100 + 0.002T^2, \quad (1b)$$

in units of $\mu\Omega$ cm and K. Within 15% (roughly the accuracy on absolute values for these small crystals), all our crystals oxygenated at 6.9 obey these expressions, in the range $130< T <300$ K. From these one can obtain $\rho_a=\rho_{\text{plane}}$, $\rho_b=\rho_{\text{plane}}\rho_{\text{chain}}/(\rho_{\text{plane}}+\rho_{\text{chain}})$, and $\rho_{ab}=(\rho_a+\rho_b)/2$ for uniformly twinned crystals.

A T^2 dependence in high-T_c cuprates has been observed for overdoped $La_{2-x}Sr_xCuO_4$ and $Tl_2Ba_2CuO_{6+y}$, as well as in the electron-doped compound $Nd_{1.85}Ce_{0.15}CuO_4$.[1] In all cases it is associated with the CuO_2 planes. Because of the one-dimensional (1D) character, the situation here is quite different. Within conventional transport theory, the origin of the T^2 behavior is more likely to be phonon scattering than electron scattering, both because of the high temperatures and the fact that in one dimension the latter yields a linear temperature dependence.[12] Empirically, it is interesting to note that the resistivity of the quasi-1D organic conductors generally obeys a T^2 dependence over much the same temperature range: for example, from 40 to 300 K for $(TMTSF)_2PF_6$. For these compounds, the T^2 dependence has been explained with phonon scattering within models based either on linear or quadratic electron-phonon coupling, found to be valid over different temperature ranges.[13] To apply such models to the Cu-O chains of $YBa_2Cu_3O_{6.9}$, information about the relevant phonon frequencies and the electronic mean free path would be needed.

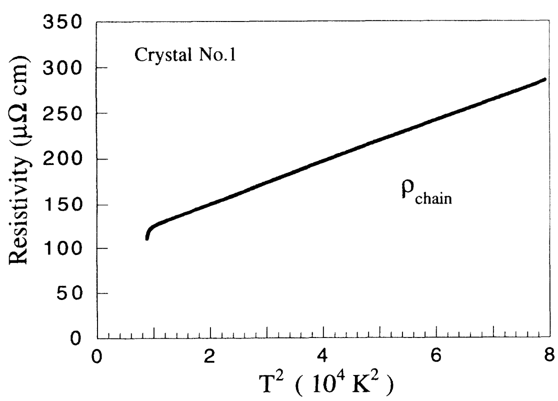

FIG. 3. The calculated chain resistivity of Fig. 2 plotted as a function of temperature squared. $\rho_{\text{chain}}(T)$ is perfectly quadratic in the range $180< T < 280$ K, with a slight downward curvature below that interval.

It is worth pointing out that the T^2 behavior of the chain resistivity is largely independent of our assumption of isotropy for transport *within* the CuO_2 planes. If instead this anisotropy is taken to be 2.0, such that $\sigma_b = (1/2)\sigma_a + \sigma_{\text{chain}}$,[14] the extracted ρ_{chain} is still found to follow a T^2 law in the same temperature interval, only with a value decreased by an overall 30%. Of course, the chains themselves are always assumed to conduct very little in the perpendicular direction.

The third feature worth noticing in Figs. 2 and 3, as in Eq. (1), is the large value of the extrapolated residual resistivity for the chains, of order 100 $\mu\Omega$ cm, as compared to zero (sometimes less) in the planes. This is not surprising given the likely disorder of oxygen vacancies in the chains, especially in crystals not fully oxygenated, combined with the stronger impact of defects on conduction in 1D. Presumably, in the absence of oxygen vacancies (δ=0), and of other defects, the chain resistivity would extrapolate to zero. In such an ideal crystal, we would expect the anisotropy ratio to reach a value of 3.0 at

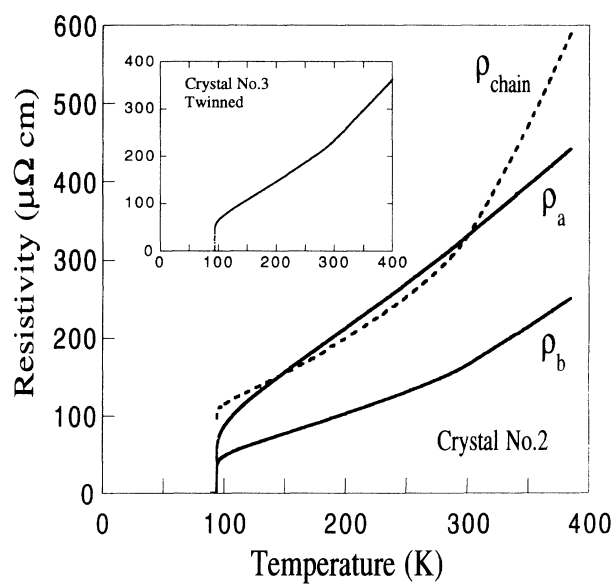

FIG. 4. Temperature dependence of the resistivity along a and b for crystal No. 2 (solid lines). Note the marked increase in slope around 300 K: It is much more pronounced for the b direction, indicating that the effect originates in the Cu-O chains, as made manifest by calculating the chain resitivity (ρ_{chain}, dashed line). Inset: resistivity of a twinned crystal over the same temperature range.

250 K. An interesting consequence of this is that even in the best crystals of $YBa_2Cu_3O_7$ currently available, electronic transport in the a-b plane is likely to be essentially isotropic in the superconducting state at low temperatures.

In Fig. 4 the temperature dependence of the in-plane resistivity is shown up to 400 K for a twinned crystal (inset), and for $\rho_a(T)$ and $\rho_b(T)$ separately. A distinct change of behavior is seen to set in around 300 K, characterized by an abrupt increase in the chain resistivity. Note also that $\rho_a(T)$ does deviate slightly from linearity at 300 K. In a twinned crystal, this feature represents a 70% increase in slope. There are only two previous reports of this: Ito *et al.*[15] briefly mention a "spurious" rise in $\rho_{ab}(T)$ occuring between 300 and 400 K, which they attribute to a rearrangement of oxygen atoms. We stress that temperatures in the range 300–400 K are too low to modify the oxygen content of the crystals, and indeed no temperature hysterisis is observed. However, oxygen mobility may well play a role, seeing as it becomes important around 300 K, at least in the oxygen-deficient ortho-II phase.[16] Goldschmidt and Eckstein[4] observed a gradual upturn in the resistivity of a ceramic sample up to 400 K, which they explain in terms of Frenkel defects in the chains. Although the thermal activation of such defects (chain vacancy-interstitial pairs) is an appealing mechanism, the chain resistivity we derive fails to agree with their assumed ρ_{chain} (set equal to $\rho_0 + \alpha T + \beta \exp[-E_d/kT]$): Quite apart from the fact that the intrinsic behavior (at low T) is quadratic, not linear, the excess resistivity above 300 K is linear, not at all exponential.

In conclusion, the in-plane resistivity of high-quality $YBa_2Cu_3O_{6.9}$ can be summarized as follows. Below 300 K the resistivity of the chains obeys a T^2 law with a large extrapolated residual resistivity ρ_0 (approximately 100 $\mu\Omega$ cm) while the resistivity of the planes is perfectly linear with negligeable ρ_0. Above 300 K, the chain resistivity increases steeply, pointing to the onset of an additional scattering mechanism, probably related to an enhanced oxygen mobility, which also affects slightly the conduction in the planes.

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