$T^2$ dependence of the resistivity in the Cu-O chains of YBa$_2$Cu$_3$O$_{6.9}$

Robert Gagnon, Christian Lupien, and Louis Taillefer

Department of Physics, McGill University, 3600 University Street, Montréal, Québec, Canada H3A 2T8
(Received 31 January 1994)

The temperature dependence of the electrical resistivity along the $a$ and $b$ axes of YBa$_2$Cu$_3$O$_{6.9}$ 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. In YBa$_2$Cu$_3$O$_{7-\delta}$ (with $\delta$ close to 0), the CuO$_2$ planes are interspaced with Cu-O chains which lie along the $a$-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 and an associated superconducting gap. 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 and in thin films—a feature already apparent in earlier work on crystals. 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$_2$Cu$_3$O$_{7-\delta}$ (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, Friedemann et al. were the first to report the separate temperature dependence of $\rho_a$ and $\rho_b$. Their two crystals were grown in yttria-stabilized zirconia (YSZ) crucibles. An anisotropy factor $\rho_a/\rho_b=2.2\pm0.2$ was obtained for $150 < T < 275$ K. Both $\rho_a$ and $\rho_b$ were reported to be linear in temperature above the fluctuation regime. For one crystal, a slight upward curvature can be seen in both $\rho_a$ and $\rho_b$ above 240 K.

The crystals were grown by a self-flux method, starting with powders of Y$_2$O$_3$ (99.9999%), BaCO$_3$ (99.9999%), 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. 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 < $\delta$ < 6.92, based on existing oxygen diffusivity studies. The oxygenated crystals were microwinned almost uniformly over their entire surface. Those with the most rectangular shapes and without macroscopic defects were chosen for detwinnning, 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 550°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, 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 $l_a'$, $l_b'$, and $l_c'$ and using the standard equations of Ref. 11, with the approximation $l_c'/\sqrt{l_a' l_b'} << 1$, where $l_a'$, $l_b'$, and $l_c'$ are the dimensions of an equivalent isotropic crystal. Because of the large $\rho_c$ (of order 5 m$\Omega$ 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, $\rho_a$ and $\rho_b$ being obtained from the same crystal. In this study, four detwinning 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 $\mu$m. 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 detwinning, 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 $\rho_{\text{tw}} = (\rho_a + \rho_b)/2$ 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, $\rho_{\text{tw}} = 190$ $\mu$$\Omega$ cm, while $\rho_a = 280$, $\rho_b = 130$, so that $(\rho_a + \rho_b)/2 = 205$ $\mu$$\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 twinned and detwinned crystals coming from different groups. The anisotropy ratio is in agreement with the value of $2.2 \pm 0.2$ previously found in the best samples$^9$.

\[ \frac{\rho_a}{\rho_b} = 2.15 \pm 0.05 \text{ at } T = 250 \text{ K}. \]

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), $\rho_a$ is found to be perfectly linear in temperature up to 300 K. On the other hand, $\rho_b$ 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 $\rho_a(T)$, 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 $\rho_{ab}$). In practice, it is easily visible only above 250 K, as seen on resistivity curves of previous reports$^5$.\footnote{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 planes and along the Cu-O chains. The chain resistivity $\rho_{\text{chain}}(T)$ is then given by $\rho_{\text{chain}} = \rho_a\rho_b/(\rho_a - \rho_b)$, where the plane resistivity is assumed isotropic with $\rho_{\text{plane}} = \rho_a$. 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: $\rho_{\text{plane}}(T)$ is linear; $\rho_{\text{chain}}(T)$ 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 description.}

![Fig. 1. Resistivity of crystal No. 1 as a function of temperature, for a current along the $a$ axis ($\rho_a$) and the $b$ axis ($\rho_b$), as obtained from the Montgomery technique. Note that $\rho_a(T)$ is perfectly linear above 130 K, while a distinct upward curvature is observed for $\rho_b(T)$. The dashed curve is the resistivity $\rho_{ab}$ of the same sample prior to detwinning.](image-url)
FIG. 2. Temperature dependence of the resistivity of Cu-O chains (ρchain, dashed curve) and of CuO2 planes (ρplane, solid curve) using ρa and ρb data of Fig. 1, within a simple model of two parallel conduction channels for the b axis. ρa is taken to be the isotropic in-plane component and ρchain = ρaρb/(ρa − ρb).

expressions:

\[
\begin{align*}
\rho_{\text{plane}} &= T, \\
\rho_{\text{chain}} &= 100 + 0.002T^2,
\end{align*}
\]

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\(_x\)CuO\(_4\) and Tl\(_2\)Ba\(_2\)CuO\(_{6+y}\), 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)\(_2\)PF\(_6\). 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\(_2\)Cu\(_3\)O\(_{6.9}\), information about the relevant phonon frequencies and the electronic mean free path would be needed.

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 \(\sigma_b = (1/2)\sigma_a + \sigma_{\text{chain}},\) the extracted ρchain is still found to follow a \(T^2\) law in the same temperature interval, only with a value decreased by an overall 30\%.

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 (\(\delta = 0\)), 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. 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.

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 resistivity (\(\rho_{\text{chain}}\), 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$_2$Cu$_3$O$_7$ 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.\textsuperscript{15} briefly mention a "spurious" rise in $\rho_{ab}(T)$ occurring 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 hysteresis 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.\textsuperscript{16} Goldschmidt and Eckstein\textsuperscript{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 $\rho_{\text{chain}}$ (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$_2$Cu$_3$O$_{6.9}$ can be summarized as follows. Below 300 K the resistivity of the chains obeys a $T^2$ law with a large extrapolated residual resistivity $\rho_0$ (approximately 100 $\mu\Omega$cm) while the resistivity of the planes is perfectly linear with negligible $\rho_0$. 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.

The authors would like to thank D.A. Bonn for useful discussions. This work was funded by NSERC of Canada and FCAR of Québec. L.T. would like to acknowledge the support of the Canadian Institute for Advanced Research and the A.P. Sloan Foundation.

\textsuperscript{14} A factor 2 is obtained assuming $\rho_{ab}$ to depend linearly on interatomic distance, and using the known lattice parameters ($b \approx 1.02a$) and pressure dependence of $\rho_{ab}$.