Normal-state transport parameters of epitaxial thin films of $YBa_2Cu_3O_{7-\delta}$

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We report on a striking correlation in the electrical transport behavior of very high-quality ($j_c \sim 3.4\times10^6$ A/cm^2 at $T=77$ K) epitaxial thin films of high-T_c Y-Ba-Cu-O in the normal state. With increasing superconducting performance, as characterized by the transition temperature, transition-temperature width, and critical current density, the resistivity ρ, and the Hall coefficient R_H, both assume remarkably simple temperature dependences $\rho=\alpha T$ and $R_H^{-1}=\beta T$ leading to a Hall mobility $\mu_H \propto T^{-2}$. The magnetoresistance at 10 T is less than $|\Delta\rho/\rho| < 10^{-3}$. We discuss an extreme two-carrier model to assess the T dependence of R_H.

The normal-state transport properties of the new high-T_c copper oxides are of much interest since they may provide some clues as to the mechanism for their superconductivity at lower temperatures. There have been numerous studies of this kind on the La-Ba-Cu-O ($\sim$40 K) and the Y-Ba-Cu-O ($\sim$90 K) perovskites, mostly in the form of sintered ceramics[1-8] but also on bulk single crystals,[9-12] and more recently, on thin, often epitaxial, films.[13,14] As expected, the transport properties of these materials vary considerably from specimen to specimen. However, during recent months, the steadily improving preparation techniques have revealed certain unexpected trends in the normal-state transport behavior. The normal-state resistivity ρ, in the a-b plane, was found to be strongly temperature dependent and in many cases a practically linear relationship was deduced with extrapolated intercepts that approach the origin at $T=0$.

While there are fewer reports on measurements of the Hall coefficient R_H in the a-b plane, it, too, appears to behave anomalously. The reciprocal Hall coefficient, a measure for the carrier concentration in a one-band model and, hence, roughly constant for simple metals, is strongly temperature dependent. Some of the experimental data follow an almost linear relationship, and, at least in a few cases,[4,10] intercept again with the origin of the graph.

These observations raise the question as to whether these properties are intrinsic or merely coincidental. In order to address this question, we have made an effort to investigate the correlation between material quality and the linearity of the temperature dependences of ρ and R_H^{-1}. Lacking a unique measure of material quality, we have chosen the most important and readily available macroscopic parameters characterizing each specimen, normal-state resistivity $\rho(T=300$ K), resistance ratio $R(T=300$ K$)/R(T=100$ K), width of the superconducting transition ΔT_c, and critical-current density j_c. We find clear correlations between these different parameters. In particular, with improving superconducting properties, the normal-state transport parameters approach a strikingly simple behavior in the form of a linear T dependence $\rho=\alpha T$ ($\alpha=0.77$ $\mu\Omega$ cm/K) and $R_H^{-1}=\beta T$ ($\beta=2.4\times10^{-6}$ cm^3/C K).

Our specimens were thin films of $YBa_2Cu_3O_{7-\delta}$ grown epitaxially on (100)-oriented $SrTiO_3$ substrates. A vacuum deposition system equipped with two electron guns and two thermal evaporation sources was used.[15,16] The deposition rate of BaF_2 is controlled by a quartz crystal monitor and the Y and Cu rates are controlled by a Sentinel III detector. During deposition, the chamber is backfilled with pure, dry O_2 gas to $5-10\times10^{-6}$ Torr. This procedure prevents segregation. All films were fabricated by depositing Y, Cu, and BaF_2 at a combined rate of $\sim$10 Å/sec onto unheated ⟨100⟩ $SrTiO_3$ substrates. After deposition the samples were annealed in a tube furnace in a slow flow (5–10 ℓ/min) of O_2 gas bubbled through H_2O. A typical annealing cycle was 15 min at 500 °C, 30 min at 800 °C (or 60 min at 700 °C), 5 min at 500 °C, followed by cooling to room temperature in 2–3 min. After annealing, the films are typically 1000–1500 Å thick and appear shiny and black in color.

For transport studies, bridges $\sim$50 μm wide and $\sim$500 μm long were photolithographically defined and etched in dilute acid. The contacts were made by fluxless indium soldering. The critical current densities at 77 K were determined in boiling liquid nitrogen and a voltage drop of 1 μV across the bridge was adopted as a criterion for loss of superconductivity. Temperature-dependent measurements were performed in a Varitemp Dewar placed inside a 10.8-T superconducting magnet. The temperature was stabilized to better than 0.1 K. Resistivity ρ and Hall resistance R_H were measured using standard lock-in techniques at a frequency of 17 Hz. Currents did not exceed 100 μA and care was taken to avoid any heating effects.

Table I lists a representative sample of the Y-Ba-Cu-O films that have been studied together with their physical and electrical parameters. The sequence was chosen to reflect descending superconducting performance with sample 1 marking our best specimen, most notable in its critical current density of 3.4×10^6 A/cm^2 at 77 K. Most of the parameters of Table I vary monotonically with position, indicating a clear trend from top to bottom. In particular, the resistance ratio $R(T=300$ K$)/R(T=100$ K), which is independent of the exact physical dimensions of the bridge, increases monotonically. Sample 2 has an anomalously low critical-current density possibly related to an undetected microscopic crack in its bridge. Figure 1 shows the temperature-dependence of the resistivity for all samples of Table I. The relationship between ρ and T is

TABLE I. Transport parameters of samples described in text and shown in Figs. 1–4.

Sample	T_c (K)	ΔT_c (K)	j_c(77 K) (10^6 A/cm^2)	$\rho_{300\,K}$ ($\mu\Omega$ cm)	$\rho_{100\,K}$ ($\mu\Omega$ cm)	$\frac{\rho(300\ K)}{\rho(100\ K)}$	μ(100 K) (cm^2/V sec)
1	92.5	0.6	3.4	233	68	3.4	34
2	91.7	0.9	0.7	214	57	3.8	17
3	90.6	1.1	1.7	215	52	4.1	15
4	92.3	1.2	1.3	198	50	4.0	14
5	89.9	2.1	0.9	173	36	4.8	10
6	88.6	2.7	0.5	151	28	5.4	11

almost linear in all cases with a tendency to slightly positive curvature for samples 3 through 6. The extrapolated intercepts, T_0, on the temperature axis increase monotonically with increasing sample number. For sample 1, the intercept coincides with the origin of the graph. Figure 2 shows the Hall voltage V_H as a function of magnetic field for sample 1 at various temperatures above and slightly below T_c. Data on all other specimens are comparable. Hall measurements were performed for both perpendicular magnetic field directions and any contributions to the Hall voltage even in magnetic field were eliminated. Above 95 K, V_H is linear and identical in both field directions from which a Hall coefficient $R_H(T)$ can be unambiguously deduced. On approaching T_c, the Hall effect develops anomalies associated with the transition to the superconducting state.[17] These will be discussed separately below.

In Fig. 3, we present Hall data on all samples of Table I in the temperature range below $T=300$ K for which the Hall voltage is strictly linear in H. In all cases, the Hall effect indicates hole conduction. Interpreting the data in terms of single-band conduction we have chosen units of $p=1/R_He$ and V_0/R_He equivalent to the carrier density per cm^3 and per unit cell $V_0=173$ Å^3, respectively. The numbering scheme follows Table I.

Figure 3 displays several striking features. The average carrier density in each sample *drops* with *increasing superconducting performance* and is temperature dependent; in most cases over the whole accessible temperature range. Samples 5 and 6 are distinct. From the growth parameters, Rutherford backscattering and x-ray scattering these samples were found to be Cu rich, containing a large fraction (70%) of another phase.[16] In samples 1–4, growth conditions were optimized and a second phase was not detectable. Extrapolating the carrier density in a crude fashion towards $T=0$, it appears that all traces would approach the origin, including the Cu-rich specimens. Such a behavior is highly unusual for a material that, from its carrier density alone, must be considered a metal. Most striking is the trace for sample 1, our highest quality specimen. Its carrier density is reproduced in Fig. 4 together with the T dependence of its resistivity and the ratio of both parameters is shown. Over most of the T range the carrier density p follows a dependence $p \propto T$.

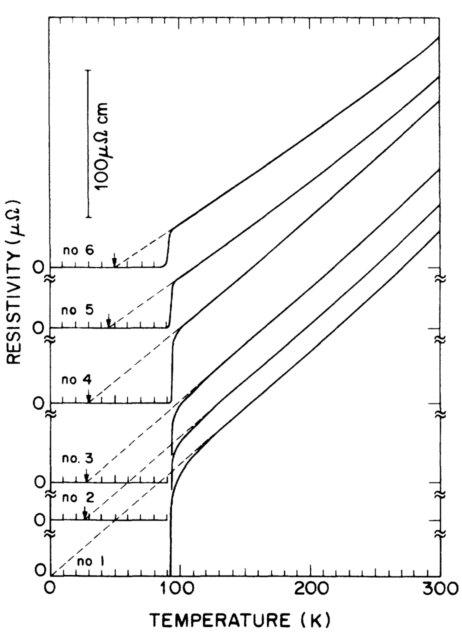

FIG. 1. Temperature dependence of the resistivity for six epitaxial Y-Ba-Cu-O thin-film specimens listed in Table I.

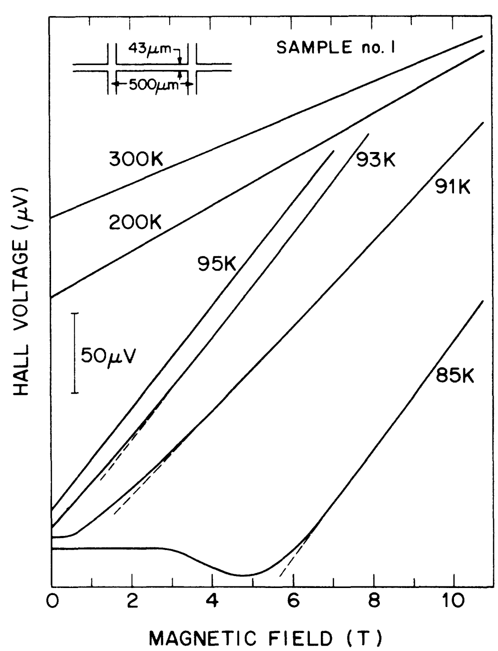

FIG. 2. Magnetic field dependence of the Hall voltage at different temperatures for sample 1 of Table I. Hall voltage vanishes at $H=0$. Traces are offset for clarity.

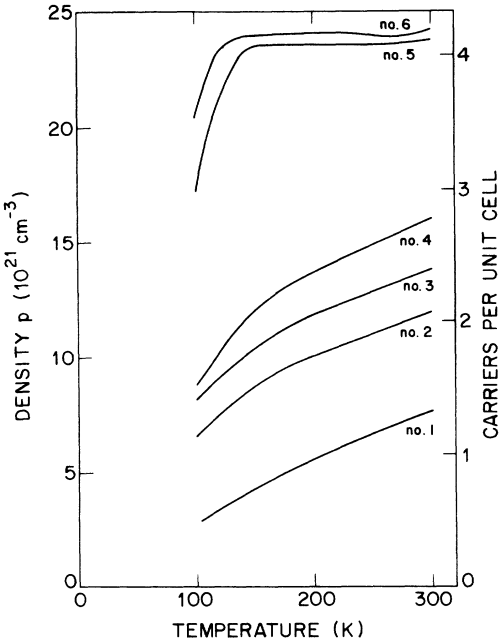

FIG. 3. Temperature dependence of the carrier density p for six epitaxial Y-Ba-Cu-O thin-film specimens listed in Table I. p was determined from the Hall coefficient R_H via $p = 1/R_H e$.

The slight deviation from such a relationship between p and T at high temperatures may be the remnant of some bowing which dominates in the lower-quality material. For the resistivity, the dependence $\rho = \alpha T$ is fulfilled within experimental error.

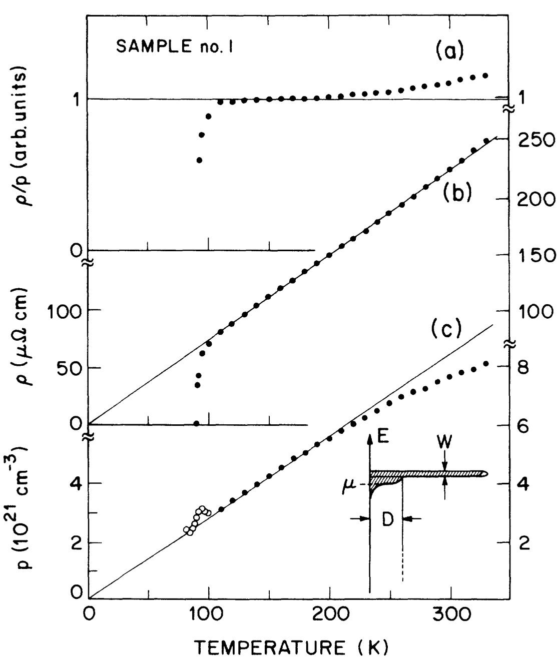

FIG. 4. Temperature-dependent transport data on sample 1 of Table I. (a) Ratio of $\rho(T)$ and $p(T)$, (b) resistivity $\rho(T)$, (c) carrier concentration $p(T)$. Open circles in (c) refer to high-field slope of the Hall voltage shown in Fig. 2. Inset shows the model band structure discussed in text.

For purposes of illustration, we plot in Fig. 4(a) the almost T-independent ratio of $\rho(T)/p(T)$. The data of Figs. 3 and 4, combined with the trends found in Table I, we interpret as striking evidence for unique temperature dependences of $\rho = \alpha T$ and $R_H^{-1} = \beta T$ of high-quality Y-Ba-Cu-O material in the normal state leading to a Hall mobility $\mu_H \propto T^{-2}$.

The temperature dependence of ρ for a simple metal usually follows such a linear relationship for $T \gg \Theta_D$ with deviations below Θ_D.[18] However, this condition for linearity is apparently not necessary in Y-Ba-Cu-O since its $\Theta_D \sim 400$ K.[19–22] In any case, a discussion of $\rho(T)$ in terms of a simple metal is not warranted in view of the strongly varying carrier concentration (see Fig. 3). This T dependence of the Hall coefficient R_H is the truly striking feature of our data. For a simple metal, we expect R_H to be practically T independent. A T-dependent R_H may either result from thermal activation of carriers or from multiband conduction. Thermally activated behavior, as observed in semiconductors, follows an exponential, not linear, T dependence. Multiband conduction is expected to lead to a nonvanishing magnetoresistance. The magnetoresistance for two-band conduction of carriers having densities p_h and p_l effective masses m_h and m_l and mobilities μ_h and μ_l ($\mu = e\tau/m$) is[23]

$$\frac{\Delta\rho}{\rho} = \frac{p_l p_h r}{(p_l + p_h r)^2}(1-r)^2 \mu_l^2 H^2 ,$$

where $r = \mu_h/\mu_l$ and h and l refer to heavy and light carriers respectively. A careful study of $\rho(H)$ on sample 1 at $T = 120$ K in fields up to 10.8 T yields an upper bound of $|\Delta\rho(H = 10.8\ \mathrm{T})/\rho(H = 0)| < 10^{-3}$. Yet, with carrier mobilities of $\mu \approx 10$ cm^2/V sec in our specimens, magnetoresistance data do not provide a stringent test for multiband conduction; e.g., for sample 1 at 100 K $\mu_l \simeq 30$ cm^2/V sec, $H = 10$ T and $p_l = p_h$ the maximum $\Delta\rho/\rho$ never exceeds $\approx 10^{-4}$ for any μ_h according to the above expression. Hence, the magnetoresistance results cannot rule out two-carrier conduction.

However, in order to generate $R_H \propto T^{-1}$, the mobilities and densities of a multicarrier system must follow rather extraordinary T dependences and interdependencies. Here, we speculate on an *ad hoc,* extreme scenario. We consider model density of states consisting of an extremely narrow band of width $W \ll k_B T$ ($T \sim 100$ K) and a carrier capacity P, coincident with the top of a quasi-two-dimensional hole band of constant density of states D (see inset Fig. 4). Densities of states having narrow bands in the vicinity of the Fermi energy of Y-Ba-Cu-O have been discussed earlier[2] in connection with one-dimensional Cu-O chains. Furthermore, band-structure calculations suggest the existence of such sharp structures close to the Fermi energy.[24,25] In all cases, however, these spikes are embedded in a much wider set of bands. Our model requires specifically the coincidence of the singularity with the abrupt end of a rather flat density of states. The chemical potential is assumed to remain in close vicinity of the narrow band. Disregarding the transition to a superconducting state for the moment, at $T = 0$, all carriers would reside within the heavy band, filling some fraction of its total capacity. At finite temperatures, thermal excitation yields a light band-carrier density $p_l = Dk_BT \times \ln[1+\exp(\mu/k_BT)]$, where the chemical potential μ can be a strong function of temperature due to the vicinity of the singularity. The Hall coefficient for two-band conduction of carriers is[23]

$$eR_H = (p_l + p_h r^2)/(p_l + p_h r)^2 .$$

For the very large mass difference and, hence, mobility ratio of our model density of states, R_H is completely dominated by the lighter species and reflects only *its* density $p_l = (eR_H)^{-1}$.

We examine the model quantitatively and find that it can indeed reproduce the *magnitude* and *linearity* of p in sample 1 of Fig. 3. This success is due to a regime for values of P and D in which μ varies essentially linearly with T. As an initial investigation of this regime, we set the total carrier specific heat in the model equal to that deduced from the reported values of the specific-heat discontinuity at T_c, interpreted in the weak coupling limit.[19–22,26] The resulting fit requires $D = 4.3\times10^{19}$ $\text{meV}^{-1}\,\text{cm}^{-3}$ and $P = 3.7\times10^{25}$ cm^{-3}. If we interpret the constant density of states as resulting from a pair of two-dimensional systems per unit cell (two Cu-O layers) this value for D corresponds to an effective mass $m_l \sim 6$. The value for P corresponds to $PV_0 = 6400$ heavy carriers per unit cell, an obviously nonphysical number given this interpretation. If the mass of the light carriers is allowed to increase, the model finds a decrease in the required number of heavy carriers roughly following $m_l^{2/3}\ln(PV_0) = 30$, for m_l up to ~ 20, above which $PV_0 \sim 70$ per unit cell, independent of m_l. As such, although an extreme multiband model can qualitatively account for the striking linearity of R_H^{-1}, quantitative considerations would require an unconventional interpretation for the huge reservoir of heavy carriers at the top of the quasi-two-dimensional hole band.

Finally, we return to the anomalies in the Hall resistivity in Fig. 1 for $T < 95$ K. They are evidently related to the superconducting transition, probably indicating fluctuation into the condensed state around T_c and inhomogeneities in the internal field distribution in this geometry. In fact, these anomalies have become a very sensitive, phenomenological tool to identify traces of higher-T_c materials in an otherwise lower-T_c material.[15] At large magnetic fields, the Hall voltage returns to linearity. The slope of this linear portion interpreted in terms of a carrier density has been incorporated in Fig. 4(c) as open circles. Although their position deviates from the linear extrapolation of the above-T_c results, their value remains in its general vicinity. With higher magnetic fields, one may be able to deduce the slope of $V_H(H)$ with higher precision and/or follow the Hall effect down to lower temperatures.

In summary, our temperature-dependent transport measurements on thin epitaxial films of YBaCuO have revealed a striking correlation. With increasing superconducting performance, the resistivity and Hall resistivity *both simultaneously* assume remarkably simple temperature dependences $\rho = \alpha T$ and $R_H^{-1} = \beta T$. The precision to which the linear relationship of the resistivity is obeyed is astounding. The Hall effect, however, is also very unusual, suggesting a linear dependence of the carrier density on T. An extreme model for two-carrier conduction is able to reproduce the striking linearity of the reciprocal Hall coefficient with temperature, although quantitative considerations require an unconventional interpretation of the carrier reservoir.

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