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Experimental test of the T^2 law for the Hall angle from T_c to 500 K in oxygen-reduced $YBa_2Cu_3O_{6+x}$ crystals

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In both "90-K" and "60-K" $YBa_2Cu_3O_{6+x}$ crystals, we find that the T^2 law for the Hall angle, measured with field $\mathbf{H}\|\mathbf{c}$, remains valid for temperatures T between T_c and 500 K. The persistence of power-law behavior over this wide range is not affected by oxygen reduction. In contrast to this anomalous behavior, the Hall coefficient observed with $\mathbf{H}\perp\mathbf{c}$ is *negative and temperature independent.* Measurements of the in-plane resistivity ρ_{xx} to 500 K disclose the existence of a kink temperature T_K ($\sim$320 K) that separates a high-temperature power-law regime from a low-temperature region in which ρ_{xx} displays significant curvature.

A central problem in the superconducting oxides is understanding the decrease of the charge degrees of freedom as we approach the "parent" insulating state.[1] In $La_{2-x}Sr_xCuO_4$, Hall measurements[2] and far-infrared reflectivity estimates[3] of the Drude weight confirm that the carrier density n shrinks continuously as the parent compound is approached ($x_{Sr}\rightarrow 0$). The decrease in n is linear in x_{Sr} for $x_{Sr}<0.14$. In the opposite limit, as x increases beyond 0.2, the electronic structure presumably recovers the Fermi surface (FS) with the full Luttinger volume corresponding to 1 itinerant electron per Cu ion. In the superconductors $Bi_2Sr_2CaCu_2O_8$ and $YBa_2Cu_3O_7$ (YBCO), angle-resolved photoemission experiments[4] observe a FS consistent with local-density-approximation calculations.[5] Nonetheless, the apparent agreement leaves unanswered the central question of what happens to the FS as the insulating limit is approached (by oxygen reduction in YBCO). Does the FS vanish abruptly, or does its volume shrink continuously? Attempts to follow changes in n with the Hall effect have not been as successful in $YBa_2Cu_3O_{6+x}$ because the Hall coefficient R_H displays an anomalous temperature dependence[6] that reflects the highly unconventional nature of the charge carriers, as well as the significant changes that occur in the electronic ground state as we move from optimum doping to the insulating phase. Thus, understanding the Hall effect anomaly is especially germane to the issues discussed above.

Anderson[7] has proposed that the temperature dependence of R_H is caused by different temperature dependences of the Hall angle relaxation rate $1/\tau_H(\sim T^2)$ and the transport relaxation rate $1/\tau_{tr}(\sim T)$. The prediction that in-plane impurity scattering simply adds a temperature-independent term to both scattering rates was confirmed by Chien, Wang, and Ong[8] (CWO), who found that the Hall angle θ_H behaves as

$$\cot\theta_H=\alpha T^2+\beta' , \quad (1)$$

where β' is proportional to x_{Zn} (the Zn concentration).

In this paper, we report measurements that extend the test of Eq. (1) to temperatures as high as 500 K. In addition, we have reduced the oxygen content in YBCO to see if Eq. (1) remains valid as the hole population is reduced. Both tests are for the geometry in which the applied field $\mathbf{H}$ is normal to the plane. By tilting $\mathbf{H}$ parallel to the plane, we also examine whether the anomalous scattering persists when the Hall current is parallel to the c axis. [In this geometry, the current ($\mathbf{I}\perp\mathbf{H}$) is applied parallel to the a-b face plane, so that the Hall field $\mathbf{E}_H$ is parallel to $\mathbf{c}$.] As-grown, microtwinned "90-K" crystals were converted to the "60-K" phase by quenching, after a 10-day anneal at the annealing temperature T_A. As in previous work,[9] we find that quenching results in sharp resistive transitions (<1 K width). The longitudinal in-plane resistivity ρ_{xx} and the Hall resistivity ρ_{xy} were simultaneously measured by ac lock-in amplifiers operating at 16 Hz (with a 1-mA current).[10] By comparing data from different crystals annealed at the same T_A, our estimated uncertainty for ρ_{xy} and ρ_{xx} is about $\pm 10\%$. The uncertainty in $\cot\theta_H$ is smaller ($\pm 5\%$) since the crystal thickness cancels in the ratio ρ_{xx}/ρ_{xy}.

We first discuss the Hall coefficient in the geometry with $\mathbf{H}\|\mathbf{c}$. In both 90- and 60-K crystals, we observe that R_H^{ab} (superscript indicates $\mathbf{E}_H$ is parallel to $\mathbf{a}$ or $\mathbf{b}$) continues to decrease with temperature up to 500 K (samples $A-C$ in Fig. 1). The persistence of this change is remarkable from the viewpoint of the usual Bloch-Boltzmann transport theory. In conventional metals, R_H is temperature dependent because the $\mathbf{k}$ dependence of the transport lifetime $\tau_{tr}(\mathbf{k})$ changes with temperature.[11] For transport limited by electron-phonon scattering, R_H ceases to change once the $\mathbf{k}$ dependence of $\tau_{tr}(\mathbf{k})$ ceases to change with temperature. Typically, this occurs when the temperature exceeds a fraction of Θ_D, viz. $T>s\Theta_D$, with $s\sim 0.2$ to 0.4.[11] In the transition elements, Ca, Cu, Ag, Mg, and W, $s\Theta_D$ falls in the range 50–100 K. However, the present results for YBCO show no evidence for saturation of R_H^{ab} at temperatures 80 K higher than Θ_D ($\sim$422 K). We show later, from the Hall-angle behavior, that saturation of R_H^{ab} can be excluded at even higher temperatures.

When we align the magnetic field parallel to the planes, we find that the behavior of the Hall coefficient R_H^c ($\mathbf{E}_H$ parallel to **c**) differs strikingly from R_H^{ab}. Penney *et al.*[12] previously reported that R_H^c is negative. However, its temperature dependence is highly uncertain, because the tiny Hall signal in this geometry is sensitive to contact misalignment.[12] With the improved resolution, we find that R_H^c is practically *temperature independent* up to the Debye temperature. (See *D* in Fig. 1. At present, we have studied R_H^c in 90-K samples only.) Moreover, the value of R_H^c (-0.62×10^{-9} m^3/C) corresponds to a Hall density of 1.85 electrons per unit cell, i.e., within 8% of the carrier density one gets by assuming one itinerant electron per copper site in the planes [we note that this is equivalent to the Luttinger volume for Cu($3d_{x^2-y^2}$)-O($2p$) states in the plane]. With **H** and **I** both in the plane, the Lorentz force, generated by acceleration of carriers parallel to the plane, is directed along **c**. Thus, the Hall current involves charge transport between the planes, a process that is little understood in the cuprates. Because of the short mean free path along **c**, conduction is usually assumed to proceed by tunneling between planes. [We remark that a temperature-independent R_H^c does *not* imply that the *c*-axis conductivity is either "metallic" or Drude-like. It may be shown that, when electrons exist in Bloch states within the planes, but moves between planes strictly by tunneling, R_H^c remains temperature independent, and the Hall density is close to n_{2D}, the areal carrier density in the plane.[13]] However, it seems clear that the contrasting behaviors of R_H^c and R_H^{ab} implies that the scattering mechanism (such as Anderson's) responsible for the strong temperature dependence of the latter operates only for electronic motion strictly *confined to the plane.*

Under oxygen reduction the itinerant hole density in YBCO is known to decrease to zero as x approaches 0.4. This is seen in dc resistivity as well as in infrared reflectivity measurements of the "Drude weight" (n/m_{tr}) (m_{tr} is the transport effective mass). In 60-K crystals, few measurements exist of the hall effect because of contact resistance problems. Our measurements of R_H^{ab} up to 500 K is displayed in Fig. 1 (samples *B* and *C* with $T_c=74$ and 60 K, respectively). Computing the Hall angle from ρ_{xy} and ρ_{xx}, we find that $\cot\theta_H$ varies linearly with T^2 in all samples (Fig. 2). The magnitude of $\cot\theta_H$ is reproducible in different crystals (compare *A* and *A'*, and *B* and *B'*). Thus, the main effect of oxygen reduction is to rescale R_H^{ab} and $\cot\theta_H$, without changing their form (at least above 100 K). Near 320 K in all samples, there occurs a slight change in slope of 10% to 14% that reflects the "kink" in ρ_{xx} previously observed.[11,14]

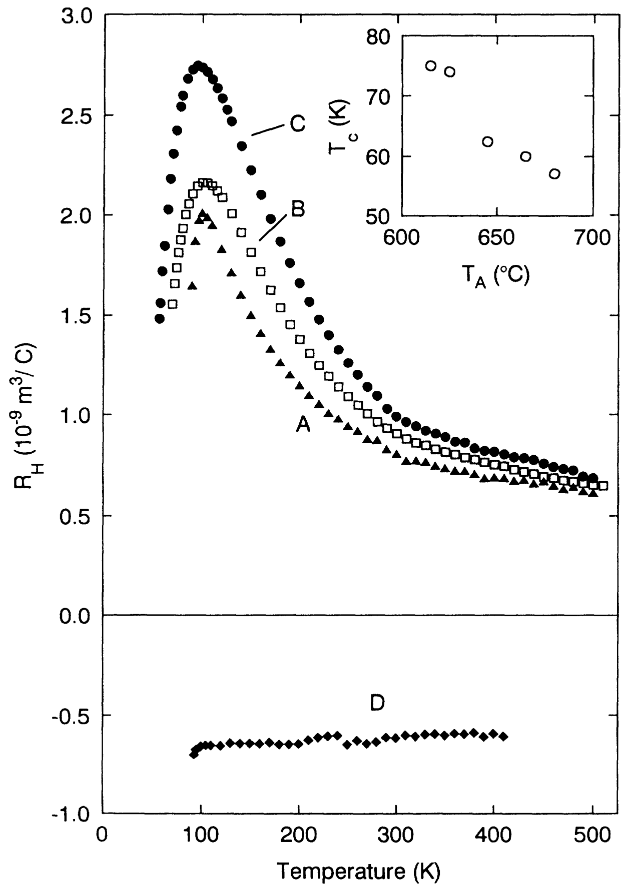

FIG. 1. The temperature dependence of the Hall coefficient in $YBa_2Cu_3O_{6+x}$ single crystals, with **H**∥**c** (samples *A*, *B*, and *C*, upper panel), and with **H**⊥**c** (sample *D*, lower). In *D*, the Hall field $\mathbf{E}_H$ is parallel to **c**. Samples *A* and *D* are as-grown crystals with $T_c=91$ K, whereas samples *B* and *C* ($T_c=74$ and 60 K, respectively) were quenched from T_A. The inset shows how T_c varies with the anneal temperature T_A.

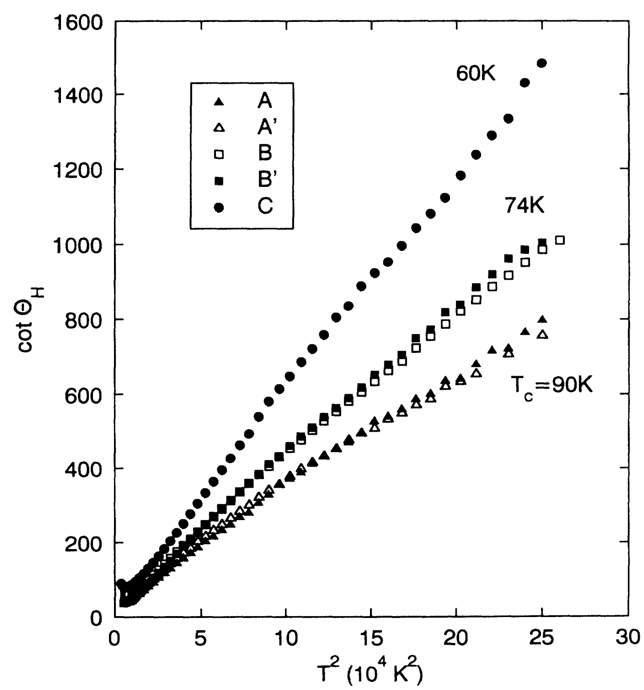

FIG. 2. Plot of $\cot\theta_H$ vs T^2 for five samples, *A*, *A'*, *B*, *B'*, and *C*. The T_c's are 91 (*A* and *A'*), 74 (*B* and *B'*), and 60 K (*C*). The uncertainty in determining $\cot\theta_H$ is about ±5% for a given *x*. The data fit well to Eq. (1) to temperatures 80 K above the Debye temperature. The slight break in slope near $T=320$ K reflects the kink in the resistivity (see Fig. 3).

The linear variation of $\cot\theta_H$ vs T^2 confirms that Eq. (1), in fact, holds in both 90 and 60 K YBCO. This has two important implications. First, the measurements confirm that the in-plane Hall-angle response is describable by a single lifetime τ_H that varies at $1/T^2$ up to 500 K. (The absence of discernible deviation from a straight line at high temperatures implies that the T^2 dependence actually extends to temperatures much higher than 500 K. This suggests the intriguing possibility that $R_H^{ab} \sim \rho_{xx} \tan\theta_H$ may not approach a finite constant at any accessible temperature.) Second, oxygen reduction does not alter the T^2 dependence of $\cot\theta_H$, aside from changing the slope α. Measurements[15] on the resistivity anistropy of untwinned crystals appear to indicate that holes in the chain states are mobile, and form a separate band which is depleted by oxygen reduction. However, the present Hall measurements show that the actual scenario is more interesting. If the second band contributes a separate Hall current, we should not observe the persistence of the power-law behavior in $\cot\theta_H$. For instance, in sample *C* ($T_c \sim 60$ K) the chain band has a population much smaller than in sample *A*. Yet, $\cot\theta_H$ has the same T^2 dependence (up to a scale factor) in both samples up to 500 K. The robustness of the T^2 behavior indicates that the chain band contributes a negligible Hall current, i.e., either the chain bands are essentially one dimensional or they do not exist. The observed anomalous Hall scattering is associated entirely with a single band of carriers, which lie in the CuO_2 plane. This inference agrees with the absence of evidence for anomalous scattering when $\mathbf{E}_H$ is parallel to **c** (sample *D* in Fig. 1).

In the test of Eq. (1) using Zn-doped YBCO, CWO (Ref. 8) showed that the slope α is unchanged whereas β' increases linearly with x_{Zn}. The data here, by contrast, show that β' remains small even for the 60-K sample, while α increases with decreasing oxygen content. If we interpret Fig. 2 in terms of Anderson's theory, an increase in α corresponds to a decrease in the energy scale W_s of spin excitations (as determined by the method of Ref 8, W_s equals 1050 K in sample *A* and ~ 850 K in sample *C*). If we identify W_s with the bandwidth which is proportional to the superexchange *J*, no change in W_s is expected.[7] Lacking a theory for how oxygen affects W_s, we may take W_s to be the experimentally determined energy scale that controls temperature dependence of the in-plane Hall coefficient.

We turn next to the in-plane resistivity (Fig. 3). All samples show a kink at $T_K \sim 320$ K that separates two distinct regimes.[11,14] Whereas the resistivity in all reduced samples displays strong curvature below T_K, it follows a power-law above T_K ($\rho_{xx} \sim T^\gamma$, with $\gamma = 1.2 \pm 0.05$). With increasing oxygen content, the negative curvature below T_K evolves into the familiar linear-*T* behavior in 90-K samples. Thus, in YBCO, linear-*T* behavior in ρ_{xx} is confined to samples with $T_c > 90$ K (and there only for temperatures below T_K). To show more clearly the transition at T_K, we may factor out the high-temperature behavior common to all samples and plot the quantity T^γ/ρ_{xx}, which is proportional

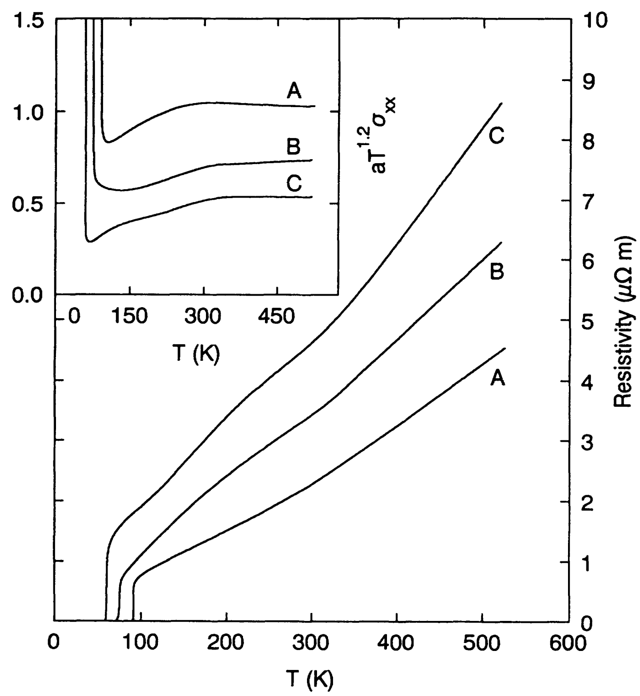

FIG. 3. The temperature dependence of the in-plane resistivity ρ_{xx} for the samples *A*, *B*, and *C* up to 520 K. In all samples, there is a broad kink that occurs at $T_K \sim 320$ K. Below T_K, ρ_{xx} displays significant curvature in samples *B* and *C*, whereas above T_K, it follows a power law T^γ, with $\gamma \sim 1.20 \pm 0.05$. The inset shows a plot of T^γ/ρ_{xx} vs *T*. The absolute value of this quantity above T_K, which is proportional to the Drude weight (n/m^*), decreases by 50% in going from samples *A* to *C*. Below T_K, there is a slow decrease of (n/m^*) reminiscent of the (corrected) bulk susceptibility (Ref. 16).

to the Drude weight (n/m_{tr}). (Comparing the relative values of T^γ/ρ_{xx} evaluated above T_K for all samples, we find that they decrease with T_c, as expected of the Drude weight.) Below T_K, T^γ/ρ_{xx} decreases smoothly with temperature (inset in Fig. 3). The amount of decrease is largest in the 60-K crystal, but is evident in the 90-K crystal as well. Does this decrease reflect a subtle change in the electronic structure, or an increase in the scattering rate $1/\tau_{tr}$ that begins at T_K? The available evidence favors the former. From susceptibility measurements of Johnston *et al.*,[16] the "corrected susceptibility" χ_{cor} displays a change of slope near T_K quite similar in shape to the curves in the inset of Fig. 3 ($\chi_{cor} = \chi_g - C/T$, where C/T is the Curie tail from impurities). These anomalies in χ_{cor} are most evident for $x > 0.9$, but are discernible for *x* as small as 0.5. Weak anomalies are also observed in the specific heat at T_K in the 90-K phase.[17] The evidence indicates that, at T_K, a broad transition (or crossover) occurs, leading to linear-*T* resistivity in $YBa_2Cu_3O_7$, but a markedly curved resistivity profile in the reduced samples. Despite these changes at T_K, the $\cot\theta_H$ behavior is not affected, except for a slight change in the slope. (A plausible origin of the kink at T_K is oxygen ordering in the chains. As far as we know, no scattering evidence exists to indicate that the ordering is abrupt, or that it occurs near 320 K. Moreover, the ordering transition temperature is predicted[18] to be very sensitive to the oxygen content x, whereas our data, and that of Ref. 14, show that T_K is almost *independent* of x. In our opinion, this insensitivity in the crucial range $0.5 < x < 0.95$ strongly argues against such a simple origin.)

In summary, we have measured how ρ_{xx} and ρ_{xy} behave at temperatures up to 500 K in single crystals of $YBa_2Cu_3O_{6+x}$. In both the 90- and 60-K phases, the inplane Hall angle involves a scattering rate that varies as T^2 up to 500 K. The persistence of the power-law behavior suggests that R_H^{ab} may not approach a finite value in the high-temperature limit. Reducing the oxygen content increases both R_H^{ab} and $\cot\theta_H$, but their general temperature dependence above 100 K is not significantly altered. This suggests that the chain bands contribute little to the in-plane Hall current. In contrast to the anomalous inplane transport, the Hall coefficient in 90 K YBCO with the Lorentz force parallel to **c** is temperature independent. The value of R_H^c suggests that the density of carriers participating in c-axis conduction is close to one per Cu(2), and negative in sign. These sharp differences point to qualitatively distinct transport mechanisms normal to the planes, compared with the in-plane direction.

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