Effect of Zn Impurities on the Normal-State Hall Angle in Single-Crystal $YBa_2Cu_{3-x}Zn_xO_{7-\delta}$

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In Zn-doped single-crystal $YBa_2Cu_{3-x}Zn_xO_{7-\delta}$ we show that the normal-state Hall angle varies as $\cot\theta_H = \alpha T^2 + \beta x$, as predicted by Anderson (T is temperature). The existence of two distinct relaxation time scales ($\tau_H \sim 1/T^2$ and $\tau_{tr} \sim 1/T$), required by experiment, precludes all multiband Drude-type models. A number of puzzling features of the Hall effect in the cuprates are resolved with the new analysis. We also report an improved measurement of the scattering cross section of Zn in the CuO_2 planes.

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Among the normal-state transport properties of the high-temperature cuprate superconductors, the Hall effect remains one of the hardest to explain [1]. In the majority of the hole-type cuprates the Hall coefficient R_H falls monotonically with increasing temperature, even above 300 K. The most striking temperature dependence occurs in 90-K $YBa_2Cu_3O_{7-\delta}$ (YBCO) [2,3]. The R_H vs T profile in untwinned YBCO crystals is very similar to that in twinned crystals [4]. With improving crystal quality, the temperature dependence in $Bi_2Sr_2CaCu_2O_8$ (Ref. [5]) and $La_{2-x}Sr_xCuO_4$ (for x near 0.15) [6] now approaches that of YBCO. Polycrystalline samples of the thallium cuprates [7,8] also display a monotonically decreasing R_H vs T. The pronounced temperature dependence of R_H stands in sharp contrast to the behavior of R_H in conventional metals with complicated Fermi surfaces (FS) such as Cu, Ag, W, Mg, and Ca. In these elements, R_H invariably becomes insensitive to temperature when the temperature exceeds $s\Theta_D$ (where $s \sim 0.2$–0.4 and Θ_D is the Debye temperature) [3,9]. In a recent study on microtwinned YBCO crystals, Chien *et al.* [3] found that the origin of the unusual Hall behavior resides in the Hall *conductivity* σ_{xy}, which is fitted well by the power law $1/T^3$ between 95 and 360 K. The $1/T^3$ power law is particularly awkward to accommodate in the usual multiband Boltzmann-Bloch scheme. Yet another puzzling feature of the Hall effect is the sensitivity of the anomalous temperature dependence to in-plane disorder. Clayhold *et al.* [10] found that the suppression of T_c by Zn or Co impurities in polycrystalline YBCO is correlated with suppression of the "Hall slope" $d(1/eR_H)/dT$. A similar correlation is observed in $La_{2-x}Sr_xCuO_4$ when the Sr content is altered [6] and in $Tl_2Ba_2CaCu_2O_{8-\delta}$ when the oxygen content is tuned [8].

Anderson [11] recently proposed a way to understand the Hall anomaly in the pure system by distinguishing relaxation rates for carrier motion normal to the FS and parallel to it (i.e., along $\mathbf{v}_k \times \mathbf{H}$, where $\mathbf{v}_k$ is the velocity at the FS and $\mathbf{H}$ the field). The theory makes a specific prediction on how the Hall angle behaves when in-plane impurities are introduced. We report experiments on Zn-doped crystals of YBCO that confirm the prediction, and show that a transparent pattern emerges when the Hall results are plotted as Hall angles. The new perspective gained explains in a convincing way the sensitivity of the Hall slope to impurities. These experiments also allow an improved determination of the scattering cross section of Zn in the CuO_2 plane.

In YBCO, the transport scattering rate $1/\tau_{tr}$ that appears in the resistivity is linear in T above the transition temperature T_c, viz. $\hbar/\tau_{tr} = \eta k_B T$, with $\eta \approx 2$ [12]. In the usual quasiparticle picture (we consider one band in the weak-field limit), σ_{xx} is proportional to τ_{tr}, whereas $\sigma_{xy} \sim \tau_{tr}^2 \sim 1/T^2$. In Anderson's theory, the transverse ("Hall") relaxation rate $1/\tau_H$ is determined by scattering between spin excitations alone, and goes as T^2. Thus, σ_{xy} is proportional to $\tau_H \tau_{tr} \sim 1/T^3$. Scattering off magnetically active impurities introduces additive terms to the two distinct rates. For the transverse scattering rate, we have [11]

$$1/\tau_H = T^2/W_s + 1/\tau_M , \qquad (1)$$

where W_s is the bandwidth of the spin excitations (the spin exchange energy J in the theory) and $1/\tau_M$ is the impurity contribution. Since the Hall angle $\theta_H = \tan^{-1}(\sigma_{xy}/\sigma_{xx})$ involves $1/\tau_H$ only, Eq. (1) implies that

$$\cot\theta_H = 1/\omega_c \tau_H = \alpha T^2 + C , \qquad (2)$$

where $\omega_c = eB/m_s$, m_s an effective mass, and C is the impurity contribution. Equation (2) shows that the Hall *angle*, rather than R_H, is the most incisive probe of the anomalous effect because it does not involve τ_{tr}.

To test Eq. (2), we have grown a series of Zn-doped single-crystal $YBa_2Cu_{3-x}Zn_xO_{7-\delta}$, with x ranging from 0.01 to 0.15. The starting Zn-doped ceramic is crushed and dissolved, in the ratio 1:5, in $BaCuO_{2+\delta}$ flux at a temperature of 1025 °C. Upon slow cooling in flowing oxygen, we recover single crystals of Zn-doped YBCO. The crystals are further annealed in an oxygen atmosphere of 3 bars to optimize the oxygen content. Scanning-electron-beam dispersive x-ray analysis (EDX) measurements on these crystals show that the distribution of Zn in the a-b face varies by less than 7%. The average value of x in the crystals determined by EDX is much smaller (by a factor of 4–5) than in the starting ceramic. The transitions at T_c (determined by resistivity and ac susceptibility) are fairly sharp for low values of x ($\Delta T \sim 0.1$ K for $x<0.05$), but may exceed 5 K when x reaches 0.11. All crystals are microtwinned, so that the in-plane quantities are averaged over the a and b directions. The Hall resistivity is measured by rotating the sample in a fixed 8-T field as described in Ref. [3]. The small sizes of the crystals (length $\sim$300–450 μm), and the nonuniformity in sample thickness t, complicate the measurements. Deviations from uniformity of the Zn distribution along **c** may also lead to distortion of the resistivity measurements. For these reasons, we performed the Hall measurements on two "Hall" crystals for each x value. The resistivity was measured on the *same* crystals using the Van der Pauw technique in a separate run. In addition to the Hall crystals, we measured the in-plane resistivities of a larger set of crystals (3–4 for x) to check for reproducibility and variability.

Figure 1 displays the temperature dependence of the in-plane resistivity ρ_a and $1/R_H$ for four values of x from 0.016 to 0.108. For comparison, a crystal with $x=0$ (Ref. [3]) is also shown. With increasing dopant content, the resistivity curves [Fig. 1(a)] are shifted upwards, so that the primary effect of Zn scattering is to add a nominally temperature-independent contribution to the transport scattering rate. However, our measurements show that the slope $d\rho_a/dT$ is altered as well by the impurity scattering. The average slope increases from 0.5 to 0.87 $\mu\Omega$ cm/K, as x increases from 0 to 0.108. This may be due to a decrease in carrier concentration, or an unsuspected temperature-dependent scattering contribution by the Zn centers. The lower panel in Fig. 1 shows the effect of Zn scattering on the Hall resistivity. As x increases, the magnitude of $1/eR_H$ is suppressed at all temperatures. In particular, the temperature dependence of $1/R_H$ appears to become less pronounced with increasing x, in agreement with Hall measurements in Ni-doped ceramics [10].

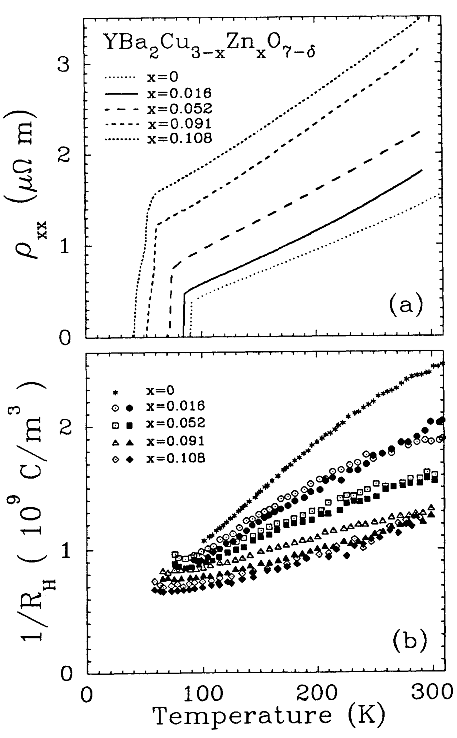

FIG. 1. (a) The temperature dependence of the in-plane resistivity (averaged over **a** and **b**) of single-crystal YBCO doped with Zn. For nonzero x, the magnitude of the resistivity at room temperature is the average of 3 to 4 samples. (b) Plot of $1/R_H$ vs T for YBCO crystals doped with Zn. In both panels, the data for the $x=0$ sample are from Ref. [3].

We turn next to the Hall angle, which is plotted as $\cot\theta_H$ vs T^2 in Fig. 2. For all samples, the data points fall on a straight line in the temperature range under $\sim$240 K, but at higher temperatures some samples show deviations. In particular, deviations of about 10% occur in the samples with $x=0.052$ and 0.091, represented by open squares and solid triangles, respectively. Above 240 K, the Hall signals are small and sensitive to thermal drifts during the measurement. We suspect this to be a serious source of error in the two samples. Data from the remaining samples are consistent with straight-line behavior up to our highest temperature. Overall, the data in Fig. 2 provide strong support for the validity of Eq. (2), especially below 240 K. By comparing the straight-line fits with Eq. (2), we find that, at 8 T, $\alpha=5.11\times10^{-3}$. The impurity contribution C increases linearly

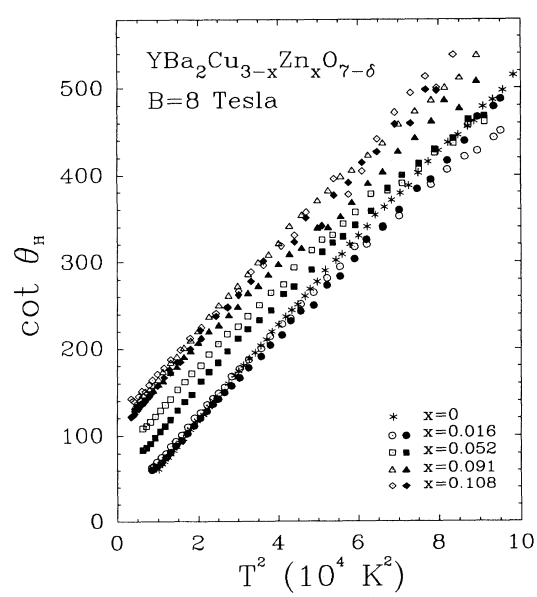

FIG. 2. Temperature dependence of the Hall angle shown as $\cot\theta_H$ vs T^2 for a series of Zn-doped YBCO crystals. $\cot\theta_H$ is computed from ρ_{xy} and ρ_{xx} measured on the same crystal. A fit by $\cot\theta_H=\alpha T^2+\beta x$ gives $\alpha=5.11\times10^{-3}$.

with x with a slope $\beta \equiv C/x$ equal to 1140 (Fig. 3).

Scattering off the Zn impurities increases both $1/\tau_H$ and $1/\tau_{tr}$. As shown in Fig. 3(a), the "residual resistivity" ρ_0 increases linearly with x (for $x<0.07$) at the rate $d\rho_0/dx=670$ $\mu\Omega$ cm. In terms of two-dimensional (2D) resistance, we have $\Delta\rho_0=227$ $\Omega/\square$ for 1% of Zn in the plane [13]. It is interesting to compare this number with the unitarity limit. For 2D systems, the resistivity due to s-wave scattering is $\Delta\rho_s=4(\hbar/e^2)(n_{imp}/n)\sin^2\delta_0$, where n_{imp} is the impurity concentration and δ_0 the phase shift. Chemical doping and reflectivity studies show that the carrier density n in the planes is 2.9×10^{21} cm^{-3} or 0.25 hole per Cu(2). If we take this n, the value of $\Delta\rho_s$ in the unitarity limit ($\delta_0=\pi/2$) equals 656 $\Omega/\square$ per 1% impurity. Thus, the resistivity is observed to change with x at $\sim\frac{1}{3}$ the unitarity-limit rate. Each Zn ion presents a scattering cross section of diameter 4.2 Å to the charge carriers, i.e., a circle around the Cu(2) site encompassing its four oxygen neighbors [13]. This rather large scattering may relate to the rapid suppression of T_c [Fig. 3(a)]. The change in ρ_0 translates into a transport scattering rate which changes by $\Delta(1/\tau_{tr})=1.1\times10^{13}m_e/m_{tr}$ s^{-1} per 1% Zn (m_{tr} is the transport mass). This is to be compared with the change in the Hall scattering rate $\Delta(1/\tau_H)=3.2\times10^{13}m_e/m_s$ derived from β. Before comparing quantitatively our results with Anderson's theory, we remark that the simple dependence of θ_H on T and x in Eq. (2) places constraints that seem to preclude models in which τ_H and τ_{tr} are assumed equal (to within a multiplicative constant) [14].

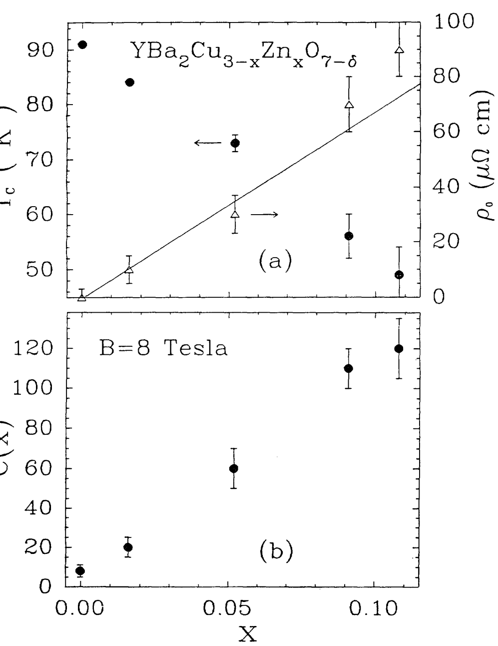

FIG. 3. (a) Variation of the T_c (circles) and the "residual resistivity" ρ_0 (triangles) with Zn content x in Zn-doped YBCO crystals. The line suggests that ρ_0 increases slightly faster than linear when x exceeds $\sim$0.07. (b) Variation with x of the impurity contribution C to $\cot\theta_H$ in the same crystals. The slope β equals 1140.

In Anderson's theory [11], the bandwidth W_s is of the order of J. To relate the coefficient α in Eq. (1) to W_s, we write θ_H as $(B/n\phi_0)k_F v_k \tau_H$ (where k_F is the Fermi wave vector, $\phi_0=h/e$, and $n=k_F^2/2\pi$). Using Eqs. (1) and (2), and $v_k\approx W_s/\hbar k_F$, we derive

$$W_s=k_B(n\phi_0/\alpha B)^{1/2}. \quad (3)$$

The experimental value of α determines W_s to be $\sim$830 K. This is of the order of $J\sim1400$ K, in agreement with Anderson's estimate. The magnitude of W_s sets the scale for the Hall effect, which we briefly discuss. The Hall scattering rate in the pure system may be written as $1/\tau_H k_B T\approx T/W_s$, which is less than 1 for all temperatures of interest (in contrast to $1/\tau_{tr}k_B T$). The two scattering rates become equal near 1700 K. Thus, the pure "cyclotron" motion is relatively long-lived compared with motion that involves displacement of the FS. However, the Hall angle remains small above T_c because the "transverse" mass m_s is very large. From the assumptions leading to Eq. (3), we find that $m_s=(\hbar k_F)^2/J\approx45m_e$. Although the estimate for m_s is crude, it seems much larger than values of m_{tr} inferred from resistivity or the photoemission experiments. (Such a large mass is a direct consequence of the assumption that $W_s\sim J$.)

The striking simplification of the Hall data in going from R_H [Fig. 1(b)] to the $\cot\theta_H$ plot (Fig. 2) is, in our view, persuasive evidence that this new analysis of the Hall effect is correct. Aside from accounting for the prevalence of power laws with unusual exponents in σ_{xy} and $\cot\theta_H$ that extend beyond Θ_D, it predicts how $\cot\theta_H$ changes with impurity scattering in a rather natural way. The weaker temperature dependence of R_H in $La_{2-x}Sr_xCuO_4$ may now be understood to be a consequence of disorder in the Sr sites. [For a polycrystalline sample of $La_{2-x}Sr_xCuO_4$ with $x=0.16$, we find good agreement with Eq. (2) with $\alpha=7\times10^{-2}$ and $C=500$, compared with $C\approx5$ in pure YBCO.] It does not seem possible to get such discrepant behavior in $1/\tau_H$ and $1/\tau_{tr}$ at high temperatures in the usual kinetic-equation approach based on quasiparticles, at least in the weak-field limit. The verification of Eq. (1) by these experiments shows that the effects of strong correlation are quite apparent in transport quantities. In addition to Anderson's theory, we remark that recent calculations of the Hall effect in gauge-theory formulations of strong correlation models also obtain an anomalous suppression of the Hall angle at high temperatures [15,16].

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[13] For Zn dissolved in Cu metal, $\Delta\rho = 0.32\ \mu\Omega\,\mathrm{cm}$ per at.% of Zn. This translates into a cross-section diameter of 0.76 Å.

[14] In such models, $\cot\theta_H \equiv f(T,x)$ has the form $\{\sum_i A_i/w_i\}/\{\sum_i B_i/w_i^2\}$, where A_i and B_i are T-independent band parameters, and $w_i = 1/\tau_i$ is the transport scattering rate in band i. Equation (2) imposes the constraints $\partial f/\partial T = \alpha T$ and $\partial f/\partial x = \beta$, with α and β *both* independent of x and T.

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