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Hall angle in $YBa_2Cu_3O_{7-\delta}$ epitaxial films: Comparison between oxygen reduction and Pr doping

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We have investigated the temperature dependence of the Hall angle in oxygen-deficient and Pr-doped $YBa_2Cu_3O_{7-\delta}$ epitaxial films. The cotangent of the Hall angle follows a universal T^2 dependence in all superconducting samples, i.e., $\cot\theta_H=\alpha T^2+C$. In the $YBa_2Cu_3O_{7-\delta}$ system the slope α increases monotonically with δ while the quantity C remains almost constant. Most important, there exists a linear correlation between T_c and α. In the $Pr_xY_{1-x}Ba_2Cu_3O_7$ series both α and C increase with x. Combined with previous studies we conclude that the changes of α and C are related to two distinct mechanisms for suppressing superconductivity. While the increase of C corresponds to a reduction of mobility, the change of α reflects the variation in true carrier density.

One of the most puzzling problems in the study of high-T_c superconductors has been the anomalous temperature dependence of their normal-state transport properties.[1] Both the in-plane resistivity and the Hall number n_H are often found to be linearly dependent on T above T_c, which is inconsistent with a single-band Fermi-liquid description. Although a strong T dependence is possible in a two-band model provided that the scattering rates are different in these two bands, it requires precise cancellation between electron and hole contributions to obtain a linear T dependence. This is highly unlikely in all cuprate superconductors. Magnetic skew scattering is another mechanism that can cause a strongly T-dependent Hall effect. However, the failure to saturate the low-temperature Hall resistivity argues against such an explanation.

Recently a new way to understand the Hall anomaly was proposed by Anderson,[2] who argues that the intrinsic electronic degree of freedom in Cu-O_2 planes is decomposed into spin-$\frac{1}{2}$ chargeless spinons and charged spinless holons. The Fermi surface is formed by spinons. The relaxation rates for carrier motion normal to the Fermi surface and parallel to it are differentiated. The former ($\tau_{\rm tr}^{-1}$) is the usual transport relaxation rate. It is related to the spinon-holon scattering which leads to a linear T dependence, i.e., $\tau_{\rm tr}^{-1}\propto T$. The latter ($\tau_H^{-1}$) is the transverse (Hall) relaxation rate. It is the result of the spinon-spinon scattering which varies as T^2 like any other fermion-fermion interaction. So we have $\sigma_{xx}\propto\tau_{\rm tr}\propto 1/T$ and $\sigma_{xy}\propto\tau_{\rm tr}\tau_H\propto 1/T^3$. The cotangent of the Hall angle, σ_{xx}/σ_{xy}, becomes one of the essential quantities since it is dependent on τ_H only,

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

where α is related to the spinon bandwidth and C is a constant additive term due to magnetic impurity scattering.

Relation (1) describes rather well the Hall effect of a series of $YBa_2Cu_{3-x}Zn_xO_7$ single crystals.[3] Zn doping, which introduces a local spin-$\frac{1}{2}$ impurity[4] (bound spinon) into the Cu-O_2 plane, only changes C proportionally to x while maintaining a constant slope α. Soon the same relation was verified in oxygen-overdoped Tl cuprates,[5] $La_{1.85}Sr_{0.15}Cu_{1-x}A_xO_4$ (A =Fe,Co,Ni,Zn,Ga),[6] and $Pr_xY_{1-x}Ba_2Cu_3O_7$ (Ref. 7) systems. In sharp contrast to the complicated T dependence of ρ and n_H in different systems, Eq. (1) seems to be universal in every system with different doping levels.

All of the experiments[3,5-7] above have focused on the change of C due to doping rather than on the slope α which has been found to be insensitive to various dopings. To fully characterize the Hall effect, it would be ideal if one could understand how α and C depend on various parameters such as carrier concentration and cation doping. In this paper we report the results of resistivity and Hall measurements on a series of oxygen-reduced and Pr-doped $YBa_2Cu_3O_{7-\delta}$ (YBCO) epitaxial films. A very systematic picture emerges from our study. Equation (1) holds for every superconducting sample. What is most interesting here is that α is sensitive to carrier concentration, as predicted in Ref. 2. In the $Pr_xY_{1-x}Ba_2Cu_3O_7$ system both α and C vary monotonically with Pr concentration. However, in $YBa_2Cu_3O_{7-\delta}$ samples only α changes with the oxygen content while C remains constant. A linear correlation between T_c and α is unveiled in this series, implying a close relationship between the Hall effect and the superconducting mechanism.

All of the films were grown epitaxially on (100)$LaAlO_3$ substrates using pulsed laser deposition. Detailed information on the fabrication process can be found in Ref. 8. Film thickness ranged from 700 to 1400 Å, determined from Rutherford backscattering spectroscopy (RBS). The Pr-doped films are assumed to have the same Pr concentration as in the target. All of the films are c-axis oriented and of high quality as revealed from x-ray diffraction, RBS channeling, and electrical measurements. Oxygen reduction on a pure YBCO film was achieved by annealing at different temperatures in flowing Ar. Depending on different T_c values of our interest, the annealing temperature was chosen between 175 and 250 °C and the annealing time between 0.5 and 3 h. The initial ramping rate was 100 °C/h and the final step was furnace cooling. These reduced samples were from the same piece of a film, so their initial properties and thicknesses are identical. Because of the small quantity of material, the oxygen content could not be determined directly. However, it is known[9] that the normal-state resistivity of YBCO scales with its oxygen deficiency δ. We determined δ indirectly with this method. The samples were lithographically patterned into regular Hall bars (length $=500$ μm, width $=150$ μm) via wet etching (0.5% H_3PO_4 in H_2O). A dc four-probe method was employed to measure ρ_{xx} and ρ_{xy} simultaneously in an 8-T magnetic field which is parallel to the c axis (film normal). Errors due to probe misalignment, thermal voltage, etc., were corrected.

The temperature dependence of resistivity and the Hall coefficient for $YBa_2Cu_3O_{7-\delta}$ and $Pr_xY_{1-x}Ba_2Cu_3O_7$ series are presented in Figs. 1(a)–1(d). Our pure YBCO film has a $T_c=89$ K, $\Delta T_c=0.8$ K. Its resistivity is linear in T and extrapolates to zero at $T=0$. As δ and x increase, the linear T dependence is no longer maintained and T_c decreases gradually as is commonly observed.[7,10] Figures 2(a) and 2(b) show T_c as functions of Pr and oxygen content. The solid line in (b) is the expected T_c vs δ curve obtained from Ref. 10. In both systems the T_c variation is consistent with that obtained by other groups.[7,10] As shown in Figs. 1(c) and 1(d), the Hall effect is significantly temperature dependent in all of our samples. $1/R_H$ is linear in T in a limited T range (100–190 K) for the pure YBCO, but this linear T range vanishes quickly away from the pure YBCO.

The simultaneous measurements of ρ and $1/R_H$ enable us to calculate accurately the cotangent of the Hall angle, which is $\cot\theta_H=\rho/R_HB$. This quantity no longer depends on the film thickness since both ρ and R_H are inversely proportional to thickness. In semiconductor research, $\cot\theta_H$ is proportional to the so-called mobility parameter. In all of our data $\cot\theta_H$ is referred to the value at $B=8$ T, the field used in our measurement. As were presented in other recent studies on Hall effect,[3,5–7] we have plotted in Figs 1(e) and 1(f) $\cot\theta_H$ as a function of T^2 for the oxygen-deficient and Pr-doped series, respectively. Clearly, the $\cot\theta_H=\alpha T^2+C$ dependence is evident in every sample despite the wide variation in the actual T dependence of ρ and $1/R_H$. Most interesting, in sharp contrast to other Cu-site doped systems, the slope α *is not* a constant anymore, but varies monotonically with increasing δ and x in the superconducting phase. We also want to point out that although the T^2 dependence of $\cot\theta_H$ is apparent in Figs. 1(e) and 1(f), a careful examination indicates that the exact T^2 dependence does not extend over the whole T range ($T\leq 300$ K) of our

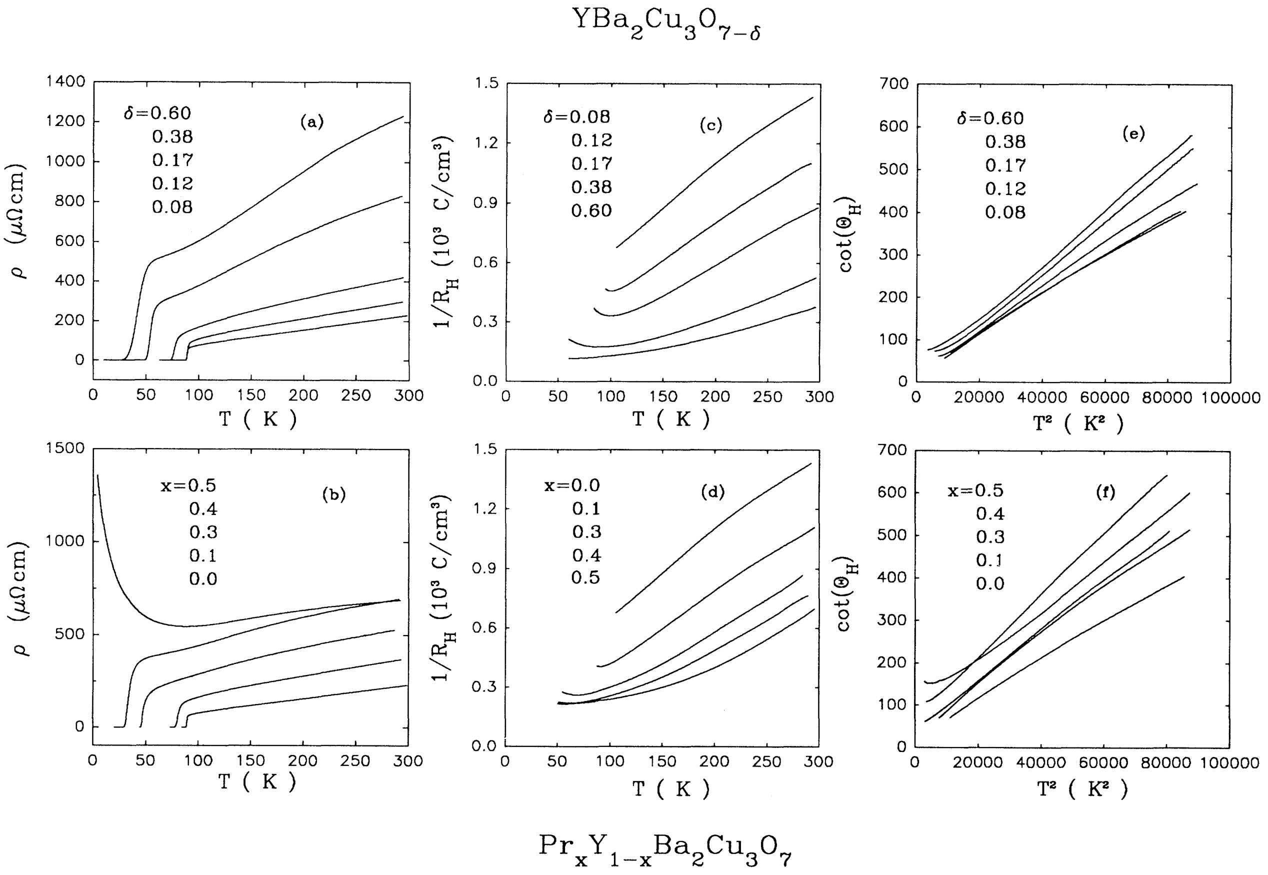

FIG. 1. (a), (b) Resistivity ρ vs T for oxygen-deficient and Pr-doped $YBa_2Cu_3O_{7-\delta}$ films, respectively. (c), (d) Temperature dependence of $1/R_H$ for oxygen-deficient and Pr-doped samples. (e), (f) $\cot\theta_H$ ($B=8$ T) vs T^2 for oxygen-deficient and Pr-doped samples.

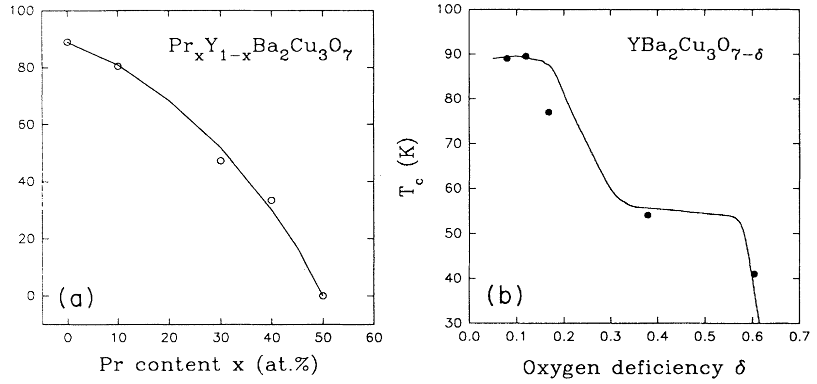

FIG. 2. (a), (b) T_c as a function of Pr content x and oxygen deficiency δ. The solid line in (b) is the expected T_c vs δ curve from Ref. 10.

study. For pure YBCO film, the T^2 dependence is observed in the range of 100–200 K, consistent with the result obtained from single-crystal samples.[3] As T_c is lowered by oxygen reduction or Pr doping, the range of the T^2 dependence moves toward higher temperatures. For example, in a sample with $T_c \cong 40$ K ($\delta \cong 0.6$), such a range becomes 170–300 K (the upper limit may be higher if not limited by our measurement). Nevertheless, the deviation from the T^2 dependence is rather small outside the range. It is intriguing that the range of linearity for the $\cot\theta_H$ vs T^2 curves increases as the superconductivity is suppressed.

Fitting the results in Figs. 1(e) and 1(f) with $\cot\theta_H = \alpha T^2 + C$ provided us with the slope α and the intercept quantity C. The α value in our pure YBCO film is nearly identical to that of pure single crystal (within 7%).[3] Figure 3 shows the variation of C with oxygen deficiency δ and Pr doping level x. Remarkably, within small fluctuations, C *does not* depend on oxygen content, but it is linear in Pr content. The latter case has been seen in other Cu-site doped systems.[3,6] The variation of the slope α is also very interesting. In Fig. 4, we plot T_c versus α. Surprisingly, T_c and α are linearly correlated with each other, indicating the close relevance of the Hall effect to the superconducting state.

Our results, together with results obtained in other systems, reveal a unified picture of Hall effect in various high-T_c cuprate systems. The behavior of $\cot\theta_H$ can be categorized into three groups: (1) varying slope α but with constant C, as in $YBa_2Cu_3O_{7-\delta}$; (2) varying C but with constant slope α, all Cu-site doped systems belong to this group;[3,6] (3) both varying α and varying C, typified by $Pr_xY_{1-x}Ba_2Cu_3O_7$. It is indeed amazing that a simple T^2 dependence of $\cot\theta_H$ is so universal in describing so many diversely doped systems. In the following we will discuss the implications of our findings.

It is well established that there exists a two-plateau $T_c(\delta)$ dependence in the $YBa_2Cu_3O_{7-\delta}$ system.[10] For $0<\delta<0.2$, T_c remains flat at ~ 90 K, then falls to ~ 60 K, exhibiting another plateau for $0.3<\delta<0.5$, and then falls to 0. This can be explained through the mechanism of hole doping into the Cu-O_2 planes by virtue of the charge reservoir.[11] On the other hand, there is a persistent controversy over the role of Pr doping in the suppression of superconductivity in the $Pr_xY_{1-x}Ba_2Cu_3O_7$ systems.[12–14] A variety of mechanisms have been proposed, including hole filling[12,13] and magnetic pair breaking.[13] The central problem has been the conflicting results on the valence state of Pr implied by different experiments.[12–14]

The new approach to analyze the Hall effect offers a different way to understand the suppression of superconductivity in these systems. In the one-band Fermi-liquid system, $\cot\theta_H$ is proportional to the Hall mobility or quasiparticle scattering rate $(1/\tau_H)$. For electron-phonon interaction, one would expect $\cot\theta_H = \alpha T + C$ according to Matheissen's rule. The current $\cot\theta_H = \alpha T^2 + C$ relation, as pointed out by Anderson,[2] may suggest that the inelastic scattering is a T^2 process, while the elastic disorder scattering still resides in C, which is supported by the fact that C is always linear with impurity concentration in many systems.[3,6,7] Impurity doping in the Cu-O_2 *planes* creates local magnetic moments[4] without affecting much of the mobile carrier density in the low doping limit. As mentioned earlier, this kind of doping preserves α but increases C linearly. Meanwhile superconductivity is strongly depressed.[3,4,6] This deterioration in T_c is mainly caused by the magnetic scattering, which reduces carrier mobility[3,6] and is pair breaking.[4]

In the $YBa_2Cu_3O_{7-\delta}$ system the situation is quite different. Here the quantity C remains constant within small fluctuations, independent of the oxygen content as shown in Fig. 3. The average C in our epitaxial films is ~ 15, compared with $C \simeq 5$ in YBCO single crystal[3] and

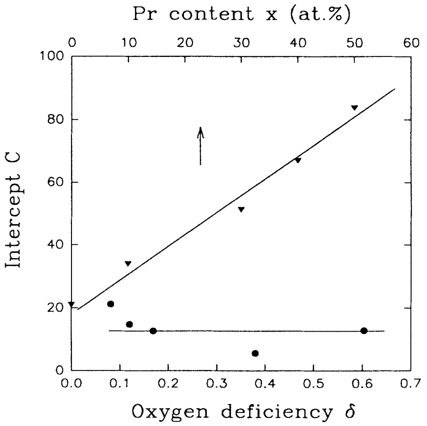

FIG. 3. The intercept quantity C vs oxygen deficiency (circles) and Pr content x (triangles). Note $B = 8$ T.

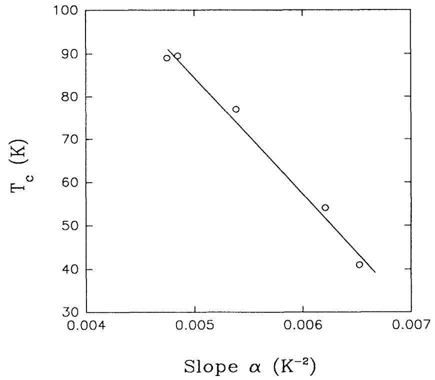

FIG. 4. The correlation between T_c and the slope α for the $YBa_2Cu_3O_{7-\delta}$ system. The magnetic field is 8 T.

$C \simeq 210$ in polycrystalline $La_{1.85}Sr_{0.15}CuO_4$.[6] The small fluctuation in C is caused by the unavoidable disorders (grain boundaries, defects, etc.) in the films. Variation in δ does not create local magnetic moments in the Cu-O_2 planes. Therefore C remains at a low value. This further supports the conjecture that C results from disorder scattering.[2] The major effects of changing δ are twofold. First, it controls the carrier (hole) density; secondly, it affects the exchange interaction J, and consequently, the dynamics of the fluctuating two-dimensional antiferromagnetic state. The only consequence on $\cot\theta_H$ brought about by the variation of δ is an increase in the slope α. This clearly tells us that the slope α is controlled by the carrier density and also possibly by the exchange parameter J. In a carrier-overdoped system, such as $Tl_2Ba_2CuO_{6+\delta}$,[5] the parameter $t\delta$ may also play an important role (t is the hopping constant) as predicted by the t-J model.[15] It is noted that in Anderson's model,[2] $\alpha \propto 1/$(spinon bandwidth). As the oxygen content is reduced, the spinon bandwidth will also be reduced, leading to an enlarged α.

The invariance of the quantity C in $YBa_2Cu_3O_{7-\delta}$ offers an important advantage enabling us to study the correlation between T_c and the slope α. If C is not constant, as in $Pr_xY_{1-x}Ba_2Cu_3O_7$, the T_c vs α relation is less meaningful because magnetic scattering embedded in C also affects superconductivity. The linear correlation between T_c and α in Fig. 4 illustrates that both T_c and α are intimately related to a same set of parameters such as carrier density and J. We believe this important correlation should be one of the essential ingredients in a viable theoretical model.

In the $Pr_xY_{1-x}Ba_2Cu_3O_7$ series, the increase of C with x indicates that the disorder introduced by the Pr doping is coupled to the electronic states in the Cu-O_2 planes. Although the Y site can be substituted by many other rare-earth elements possessing large magnetic moments, these moments do not have any effect on T_c.[16] Our results support the view that hybridization exists between Pr $4f$ states and the Cu-O_2 plane electronic states, causing the Pr magnetic moments to become effective scatterers to the electron transport. The scattering by these moments reduces the carrier mobility, which corresponds to an increase in C. The rate C/x is 108 in our Pr-doped films, but it is 1140 in Zn-doped YBCO single crystals.[3] Therefore, compared with Cu-site impurity, Pr is a much weaker scatterer. On the other hand, the increase in the slope α indicates a drop in the true carrier density just as in the case of $YBa_2Cu_3O_{7-\delta}$. Therefore our results imply that a combination of magnetic impurity scattering and hole filling is the mechanism for the suppression of superconductivity in $Pr_xY_{1-x}Ba_2Cu_3O_7$. This conclusion is supported by some other evidence,[13] but ours is reached from a completely new perspective. It is noted that Jiang *et al.*[7] also found that C increases with Pr content, but they did not uncover the systematic slope change due to insufficient resolution.

In summary, we have measured the resistivity and Hall coefficient in $YBa_2Cu_3O_{7-\delta}$ and $Pr_xY_{1-x}Ba_2Cu_3O_7$ epitaxial films. The Hall angle is found to follow $\cot\theta_H = \alpha T^2 + C$ in all superconducting samples. In the $YBa_2Cu_3O_{7-\delta}$ system, the variation of the oxygen content only affects the slope α, but not the quantity C. In the $Pr_xY_{1-x}Ba_2Cu_3O_7$ system both α and C change with Pr doping. We interpret the changes of α and C to be caused by two distinct mechanisms. The slope α is most sensitive to the carrier density while the quantity C reflects the magnetic impurity scattering in the Cu-O_2 plane. In the absence of the magnetic scattering, as in $YBa_2Cu_3O_{7-\delta}$, T_c and α are linearly correlated. The simultaneous variations of α and C with x in $Pr_xY_{1-x}Ba_2Cu_3O_7$ suggest that a combination of two effects, magnetic scattering and reduction in carrier density, leads to the suppression of superconductivity.

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