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Sign reversals in the vortex-state Hall effect in Y-Ba-Cu-O: Correlations with the normal-state Seebeck coefficient

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Superconducting-Hall-effect R_H transitions were measured on 11 $YBa_2Cu_3O_{7-\delta}$ epitaxial thin films grown under a range of electronic "doping" conditions. The data reveal that the relative magnitude of the anomalous sign reversals in R_H monotonically decrease with decreasing carrier density and vanish below a threshold cutoff value. The sign reversals in R_H are observed only in films having a negative normal-state Seebeck coefficient, and are correlated in magnitude. This suggests that the energy slope of the electronic density of states plays a role in the occurrence of these anomalies.

The anomalous sign reversals of the Hall effect near the superconducting transition temperature (T_c) have remained the source of considerable controversy for many years. These anomalies have been reported not only in the high-T_c materials but in conventional superconductors as well.[1] Moreover, recent work on amorphous Mo_3Si (Ref. 2) and MoGe/Ge multilayers[3] shows this effect to be even more general—occurring in both amorphous and isotropic, unlayered superconductors. Numerous explanations based on both intrinsic and extrinsic superconducting properties have been offered to account for these sign reversals.[1–10] Our previous data (based on studies of 11 epitaxial thin films of $YBa_2Cu_3O_{7-\delta}$) suggested an extrinsic pinning-induced backflow as the origin since the higher pinning, higher carrier concentration films showed more pronounced sign reversals.[10] Since then, Budhani *et al.* have shown that by exposing $Tl_2Ba_2Ca_2Cu_3O_{10}$ thin films to heavy ion irradiations without changing the carrier concentration (hence, keeping the electronic structure relatively constant) markedly diminishes the Hall sign reversals.[11] This finding excludes pinning-induced backflow of the vortices as the origin of this phenomenon and suggests that differences in the carrier concentration or electronic structure among our different samples may account for the enhanced sign reversals at the higher carrier concentrations. The work here correlates the magnitudes of these sign reversals to recent thermopower measurements in order to clarify the role of band structure in this general phenomenon. Understanding the origin of this effect will help strengthen the connection between band-structure features of the cuprates and the occurrence of superconductivity. More importantly, this phenomenon may even serve as a probe for detecting features in the electronic density of states near the Fermi level, discussed below.

Kunchur *et al.* recently reported mixed-state Hall data in the limit of free flux flow[12] and showed that the models based on time-dependent Ginzburg-Landau (TDGL) theory[7,8] best describe the temperature dependence of the superconducting Hall angle. Since this theory indicates that the sign reversals depend on details in the electronic band structure and not all materials should exhibit this phenomenon, we recently measured the normal-state Seebeck coefficient on nine of these same films which were processed under a range of initial "doping" conditions. Cohn *et al.* found the diffusion thermoelectric power of $YBa_2Cu_3O_{7-\delta}$ to be independent of temperature as a consequence of multiband effects.[13] Due to this relative RT independence, we selected the room-temperature thermopower as our measured parameter. Comparison of the magnitudes of the Hall sign reversals and the room-temperature thermopower demonstrates a clear relationship between these parameters. A similar correlation is also observed between the magnitude of the sign reversals and the inverse Hall coefficient (e.g., apparent carrier concentration at 100 K). This intriguing connection between the normal-state carrier concentration and mixed-state properties strongly suggests that the anomalous Hall-effect sign reversals are *intrinsic*, and likely reflect features in the electronic band structure in contrast to early work by Usui *et al.*, who suggested a connection between the sign anomaly and a different normal-state property—the electron mean free path.[1,14]

The eleven high-quality epitaxial thin films of $YBa_2Cu_3O_{7-\delta}$ were obtained either by pulsed laser ablation[15] (~2000-Å thick) or by the BaF_2 post-annealing process[16] (~1000-Å thick). The highly crystalline quality of the BaF_2 coevaporated films was subsequently verified by 2–3 % ion channeling Rutherford backscattering yields.[16] All 11 samples had superconducting transition widths (defined by 90–10 % of the normal-state resistance) of no more than 0.8 K and zero resistance transition temperatures (T_c) ranging from 88 to 92 K.[17] Figure 1 illustrates the range in resistivities produced by the various post-annealing conditions. For each film, simultaneous measurements were made of the resistivity ρ, the superconducting transition temperature T_c, and the Hall coefficient R_H, utilizing patterned bridges described elsewhere.[18] Using standard dc techniques, Hall voltages were measured at a series of fixed applied fields as a function of temperature, starting well above the transition temperature to avoid setting up flux gradients within the samples. In addition, the currents[19] were systematically reversed to eliminate thermal voltages. Afterwards, identical data-taking sequences were repeated in reversed applied fields. The Hall coefficients were obtained by taking the voltage differences of the two temperature sweeps in opposing fields to cancel the small offsets associated with slight Hall-probe mismatches. (Hall coefficients obtained by this

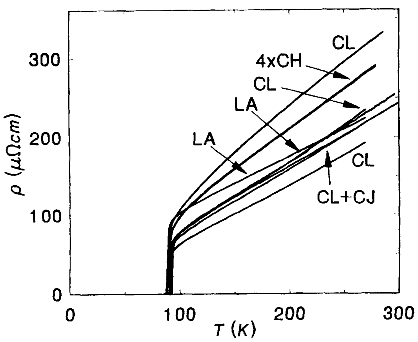

FIG. 1. Resistivity curves for the 11 epitaxial thin films of $YBa_2Cu_3O_{7-\delta}$ used in this study. The designation LA denotes growth by laser ablation, and CL, CJ, and CH indicate growth from codeposition followed by various (10^{-4} atm, 10^{-3} atm, and 1 atm, respectively) oxygen partial pressure YBCO conversion anneals. The systematic range in resistivities indicates variations in the carrier concentrations and scattering rates produced by the various growth conditions. All of the films included in this study have zero resistance transition temperatures ranging from 88 to 92 K.

method are completely consistent with determinations made by holding the temperature fixed and sweeping the field from -8 to $+8$ T.) For the Seebeck measurements, copper voltage leads and type E thermocouple junctions were attached near each end of the film with silver paste. An external heater generated a small temperature difference across the film (about 3 K). The Seebeck coefficient with respect to copper is given by the measured voltage divided by the temperature difference. The absolute Seebeck coefficient of the film is then calculated by correcting for the known Seebeck coefficient for copper.

Budhani, Liou, and Cai[11] and Kunchur *et al.*[12] have shown that flux pinning can reduce or even eliminate the Hall sign reversal anomaly. Therefore, flux pinning values were compared to the apparent carrier concentrations, $1/R_H e$, to determine the role of pinning in these doping studies. Figure 2 illustrates that as oxygen is removed from a $YBa_2Cu_3O_{7-\delta}$ thin film, reducing the apparent hole concentration, the Hall sign reversal can vanish, along with a weakening in the relative field dependence of the critical current density. In other words, as oxygen is removed from these films, the resulting decrease in the relative field dependence of the critical current densities reflects decreases in the flux pinning according to flux creep models.[20] Therefore, *increased* flux pinning alone cannot explain the disappearance of the sign reversal with the decreases in oxygen content shown in Fig. 2. Furthermore, Fig. 3(a) shows that the irreversibility line measured in six films (found from extrapolating $F_p=J_c*B$ curves to zero[21]) increases with carrier concentration along with the sign reversal magnitudes. Note that the sign reversal magnitudes are defined as the maximum applied field $B_{\max}$ where the sign reversals just exist at any temperature. This definition is chosen since the actual depth of the sign reversals depends on both the current density and the strength of the pinning, while $B_{\max}$ is relatively insensitive to these parameters.[12] Finally, both the strength of the Hall sign reversals and the strength of the pinning monotonically increase with carrier concentration, and since pinning-induced backflow of the vortices has been ruled out as the mechanism for the Hall sign reversals,[11,12] the electronic band structure remains as the key factor in this phenomenon.

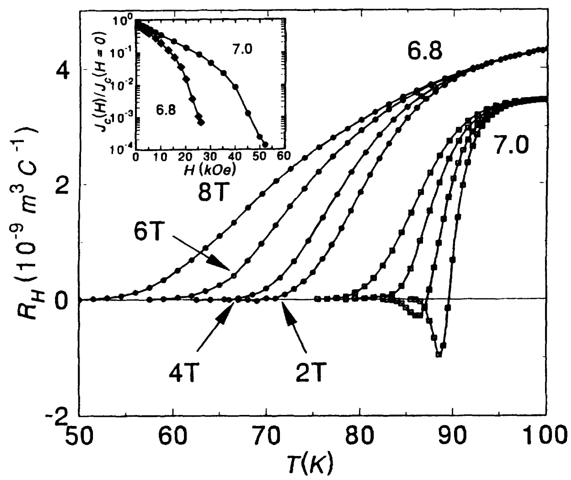

FIG. 2. Effect of carrier concentration on the superconducting Hall transitions and relative field dependence of the critical current density (inset) of $YBa_2Cu_3O_{7-\delta}$. The fully oxygenated film ($7-\delta\approx7.0$) shows the anomalous sign reversals below a cutoff field of about 5 T, whereas the oxygen-deficient film ($7-\delta\approx6.8$) shows no anomalous sign reversals. In this case, an enhancement in flux pinning cannot account for the lack of the anomalous sign reversals in these oxygen-deficient films since pinning is *always* found to decrease with oxygen deficiency. This suggests that "doping" levels influence the magnitude of the sign anomalies.

Thermopower studies were conducted to determine if differences in the electronic structure could account for the correlation between the magnitude of the sign reversals and the normal-state carrier concentration, $1/R_H e$, observed in $YBa_2Cu_3O_{7-\delta}$ [Fig. 3(a)]. In the relaxation time approximation, the diffusion thermopower is given by[22] $S=\sigma_s/\sigma$, where

$$\sigma_s=\frac{k_B|e|}{\Omega_0}\sum_{\mathbf{k}} \nu_x^2(\mathbf{k})\tau(\mathbf{k})\left[\frac{\epsilon-\mu}{k_BT}\right]\frac{\partial f}{\partial\epsilon},$$

and

$$\sigma=-\frac{e^2}{\Omega_0}\sum_{\mathbf{k}} \nu_x^2(\mathbf{k})\tau(\mathbf{k})\frac{\partial f}{\partial\epsilon}.$$

Here, $\nu_x(\mathbf{k})$ is the phase velocity on the energy surface ϵ, τ is the relaxation time, f is the Fermi function, μ is the chemical potential, and Ω_0 is the normalization volume. It can be seen that the diffusion thermopower is dependent on the energy slope of the density of states averaged over the Fermi surface. Thus, as carriers are removed from our $YBa_2Cu_3O_{7-\delta}$ thin films, the Hall sign reversals monotonically diminish and disappear at the point where the absolute Seebeck coefficient changes sign [Fig. 3(b)] suggesting that these anomalies depend on the energy slope of the density of states. Interestingly, it is possible not to observe such strong correlations because the thermopower often has significant phonon-drag contributions (manifested by a $1/T$ component above ~0.2 of the Debye temperature θ_D) that are not considered in the transport equations above. However,

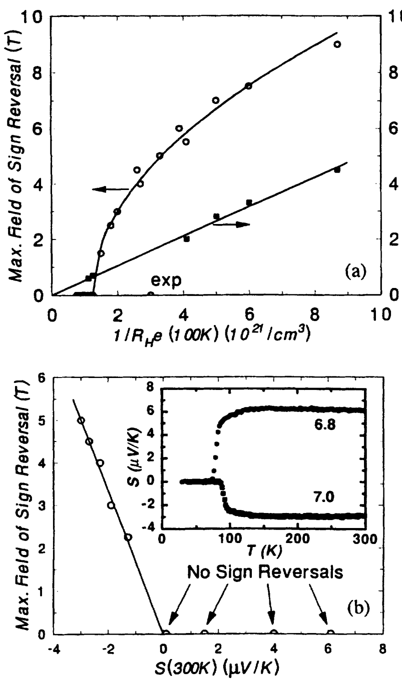

FIG. 3. The "magnitude" of the Hall sign reversals as a function of "doping." The highest applied field to which the sign reversals persist are plotted as a function of (a) Hall carrier density ($1/R_H e$) at 100 K and (b) absolute Seebeck coefficient S at 300 K. The inset illustrates the lack of phonon-drag contributions ($S_{\rm drag} \propto 1/T$) in *thin films* of $YBa_2Cu_3O_{\sim 7.0}$ and $YBa_2Cu_3O_{\sim 6.8}$ which can lead to an offset in the correlation. With the exception of the single point exp, there exists a direct correlation between the "magnitude" of the sign reversals (open circles) and carrier concentration (or Seebeck coefficient). Notice that the sign reversals disappear below a threshold carrier concentration and at the same point where the normal Seebeck coefficient changes sign. Flux pinning is ruled out as the mechanism eliminating the sign reversals since the irreversibility fields $B_{\rm irr}$ also increase with carrier concentration (solid squares).

phonon-drag effects, which may be very pronounced in $YBa_2Cu_3O_7$ single crystals,[13] are often absent in thin films [Fig. 3 (inset)] possibly as a result of increased phonon scattering in films. It is perhaps for this reason that correlations between the Seebeck coefficient and the Hall sign anomaly have not been reported previously.

Although several models[1–10] have been proposed to account for the Hall sign reversals, only the recent calculations performed in the framework of TDGL and BCS theory[7,8] predict a correlation between the electronic structure and vortex backflow. In particular, in the limit $B \rightarrow H_{c2}$, this theory gives a superconducting Hall angle

$$\tan\theta_H = \frac{R_H B}{\rho_{xx}} \approx \omega_c \tau_n + \frac{5}{2}\mathrm{sgn}(e)\zeta\left[\frac{H_{c2}-B}{H_{c2}}\right],$$

where

$$\zeta = \frac{4T}{\pi N(\epsilon_F)}\left[\frac{\partial N(\epsilon)}{\partial \epsilon}\right]_{\epsilon_F}\left(\frac{1+\lambda}{\lambda}\right).$$

Here T is the temperature, $N(\epsilon)$ is the electronic density of states, λ is the BCS pairing constant, H_{c2} is the upper critical field, τ_n is the normal-state relaxation time, and ρ_{xx} is the longitudinal resistivity. The sign of the product $\mathrm{sgn}(e)\partial N(\epsilon_F)/\partial\epsilon$ determines whether or not a sign change will be observed in the mixed-state Hall coefficient for a particular material. Therefore, our Hall sign reversal versus thermopower correlations suggest that as carriers are removed from $YBa_2Cu_3O_{7-\delta}$, the Fermi level drops through a peak in the electronic density of states, changing the sign of the density of states energy slope. This, in turn, causes the thermopower to change sign at the same point where the Hall sign reversals disappear. If this scenario is correct, the sign anomalies could reappear at even lower carrier concentrations than reported here, since band-structure calculations predict additional peaks to occur in the electronic density of states.[22]

In summary, the superconducting-Hall-effect transitions were studied in 11 epitaxial thin films of $YBa_2Cu_3O_{7-\delta}$ grown under a range of initial growth conditions. Remarkably, the data reveal a clear correlation between the anomalous sign reversals of the Hall coefficient and the normal-state properties. The relative magnitudes of the sign reversals are shown to monotonically decrease with decreasing carrier density while vanishing below a critical cutoff value. In addition, these sign reversals are shown to correlate with the normal-state thermopower—occurring only in *the films* having negative Seebeck coefficients. Enhanced flux pinning cannot explain these observations since the films having no sign reversals have a lower carrier concentration, reducing the condensation energy and flux pinning. The results are most consistent with recent time-dependent Ginzburg-Landau (TDGL) calculations[7,8] which predict that the existence of the sign anomalies depend upon the energy slope of the electronic density of states at the Fermi level.

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