

# Normal-state Hall effect in $\text{HgBa}_2\text{CaCu}_2\text{O}_{6+\delta}$ and $\text{TlBa}_2\text{CaCu}_2\text{O}_{7-\delta}$

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The normal-state Hall effect is studied in thin-film samples of the isomorphous pair of superconductors  $\text{HgBa}_2\text{CaCu}_2\text{O}_{6+\delta}$  (Hg-1212) and  $\text{TlBa}_2\text{CaCu}_2\text{O}_{7-\delta}$  (Tl-1212). A comparison of the slopes of inverse Hall mobility  $H \cot \theta_H(T^2)$ , together with a comparison of characteristic temperature  $T^*/T_c$  below which there is a systematic deviation from  $T^2$ , suggests that Hg-1212 has *twice* the charge-carrier density of Tl-1212 for samples with close to optimal  $T_c$ . This is attributed to the significant role played by the redistribution of oxygen as a result of exchanging Hg and Tl cations.

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## I. INTRODUCTION

The Hall effect in high-temperature superconductors (HTS's) in the normal state could be critical in revealing the mechanism of high-temperature superconductivity. It probes the behavior of the material's electronic structure in general and charge-carrier densities and scattering mechanisms in particular. For this reason, studies of the normal-state Hall effect have been conducted ever since the discovery of high-temperature superconductivity more than a decade ago.<sup>1</sup> A decade later, there is still no consensus as to the explanation of the observed behavior. Among these results the most famous is the existence of a temperature-squared dependence in the cotangent of the Hall angle, i.e.,  $\cot \theta_H \sim T^2$ , where  $\cot \theta_H$  is the ratio of longitudinal resistivity with transverse resistivity, or  $\rho_{xx}/\rho_{xy}$ .

To explain the unconventional Hall effect in HTS's many models have been proposed, such as magnetic skew scattering,<sup>2,1</sup> multiple bands, models in support of a spin gap or pseudogap,<sup>3</sup> and even temperature-dependent charge-carrier density.<sup>4</sup> Anderson's Luttinger-liquid model<sup>5</sup> seems to be the most popularly supported by various studies. In this model the longitudinal and transverse directions are governed by two different mechanisms and thus two different relaxation times due to spin-charge separation in the Cu-O planes. Longitudinal scattering is governed by holon-spinon interactions, with a relaxation time following a linear  $T$  dependence; transverse scattering is governed by spinon-spinon interactions, with a relaxation time following a  $\sim T^2$  dependence. Thus the longitudinal resistivity  $\rho_{xx}$  has a  $\sim T$  dependence and  $\cot \theta_H \sim T^2$ , resulting in  $n_H \sim \cot \theta_H / \rho_{xx} \sim T$ . In particular,<sup>5</sup>

$$\cot \theta_H = \frac{1}{\omega_c \tau_H} = \left( \frac{k_B^2 \phi_0}{W_s^2 B} n \right) T^2 + \beta, \quad (1)$$

where  $B$  is the applied field,  $k_B$  the Boltzmann constant,  $\phi_0 = h/e$  the flux quantum,  $W_s$  the bandwidth for the spin-spin scattering, and  $n$  the two-dimensional carrier density. The temperature-independent term  $\beta$  is due to scattering from magnetic impurities in the material.

Part of the difficulty in explaining normal-state transport properties is the complexity of the species involved. Although similar temperature dependence has been reported for the Hall angles of most HTS's the coefficients in Eq. (1) differ from system to system and sometimes even differ from sample to sample, indicating that various microstructural defects may affect interpretation of the Hall effect in HTS's. This makes it difficult to extract information about the intrinsic properties of electronic structures and charge-carrier densities in the material from the Hall-effect study.

We recently studied the normal-state Hall effect in  $\text{HgBa}_2\text{CaCu}_2\text{O}_{6+\delta}$  (Hg-1212) and  $\text{TlBa}_2\text{CaCu}_2\text{O}_{7-\delta}$  (Tl-1212) that were synthesized in a special cation-exchange process, the details of which have been reported previously.<sup>7</sup> In this process, an epitaxial Hg-1212 film was obtained from an epitaxial Tl-1212 film via Tl-Hg cation exchange at an atomic scale. A unique merit of this process is that the Hg-1212 films have nearly identical microstructures as their Tl-1212 precursor films. It should be realized that Hg-1212 and Tl-1212 have an identical crystal structure but their critical temperatures ( $T_c$ ) differ by 30 K as a result of the exchange-

TABLE I. Properties of thin films used in the Hall-effect studies. Hg-1212 films are 2000-Å thick; Tl-1212 are 1800-Å thick.

Sample	Material	$T_c$ (K)	$X$ (mm)	$Y$ (mm)
Hg (1)	Hg-1212	120	0.6	2.6
Hg (2)	Hg-1212	118	0.6	2.6
Tl (1)	Tl-1212	87	0.6	2.6
Tl (2)	Tl-1212	90	0.6	2.6

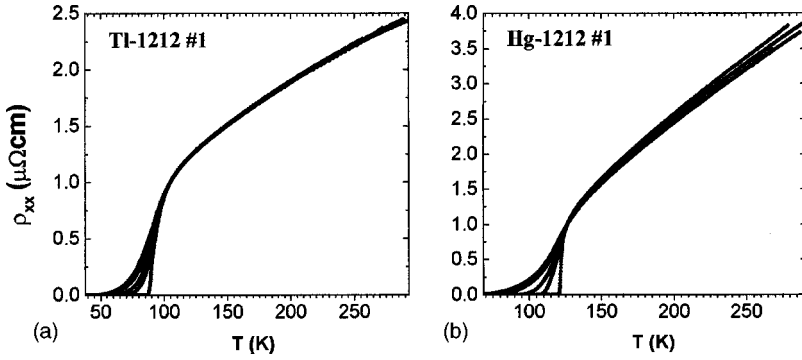


FIG. 1. Longitudinal resistivities for samples (a) TI (1) and (b) Hg (1) for applied magnetic fields 1, 2, 4, and 5.5 T.

ing of Hg and Tl cations. Hg-1212 has a  $T_c$  near 125 K and TI-1212, 90 K. Evidence<sup>6,7</sup> shows that these two species are highly isomorphic under this cation exchange. For example, the irreversibility fields ( $H_{irr}$ ) of Hg-1212 and TI-1212 were found to coincide at a reduced temperature ( $T/T_c$ ) scale.<sup>6</sup> Since  $H_{irr}$  is sensitively determined by the anisotropy of the electronic structure, one may speculate that the two systems have similar, if not identical, electronic structure. Therefore, the  $W_s$  factor in Eq. (1) is expected to be the same for the two species. This is to say that replacement of Tl cations with Hg cations may only affect the number of charge carriers in the Tl-O Hg-O planes that serve as the charge reservoir for the Cu-O planes. Since Tl and Hg cations have different valences, the oxygen distribution in this reservoir plane would be different in TI-1212 and Hg-1212. In fact, stoichiometric Hg-1212 ( $\delta=0$ ) has no oxygen in its Hg-O layer, while for stoichiometric TI-1212 ( $\delta=0$ ) the Tl-O layer is full of oxygen (one per layer). Under such an assumption, the behavior of  $\cot \theta_H$  under identical conditions would differ solely due to charge-carrier density  $n$ , since the ratio of slopes of  $\cot \theta_H$  would give the ratio by which the charge-carrier density  $n$  differs in the two species. It has already been postulated that the 30-K shift in  $T_c$  of the 1212 species is due primarily to a shift in charge-carrier density.<sup>6</sup> In examining the normal-state Hall angle, the results suggest that the  $T_c$  shift is accompanied by a doubling of charge-carrier density.

## II. EXPERIMENTAL DETAILS

The availability of high-quality film samples of both Hg-1212 and TI-1212 has made this study possible. Properties of the samples used in this study are outlined in Table I. Hg-

1212 samples were made using the cation-exchange method described in detail elsewhere.<sup>7</sup> In this process, TI-1212 films are used as a precursor by which Tl cations are replaced by Hg cations, thus ensuring the retention of the “1212” structure while cations are exchanged. This retention has been verified by Rutherford backscattering spectroscopy and x-ray-diffraction pole figures, and the process has proven highly reproducible in fabricating films of high quality. The TI-1212 samples were made using a closed-crucible process, which has been highly reproducible in producing films of good grain connectivity and purity, as described in detail elsewhere.<sup>8</sup>

Longitudinal and transverse voltages were measured by a nanovoltmeter using a five-point Hall configuration. Silver contact pads were sputtered onto the film and Pt wire leads were secured to the pads using PELCO 415 conductive silver paste, producing a noise level well within 10 nV, which corresponds to resistivity readings on the order of 1 nΩ cm. Voltage was measured at opposite currents and then averaged, with the current cycling at about 1/6 Hz. The sample stage was field cooled at an average rate of 1.5 K/min in a magnetic field of up to 5.5 T. Warming curves at the same rate were also taken and revealed the transverse and longitudinal voltages to be reversible under temperature change. At each point the voltages (already averaged over a current cycle) were measured for opposite directions of the field, thus eliminating the effect of zero-voltage offset.

## III. DISCUSSION OF RESULTS

It is tempting to compare the Hall numbers  $n_H(T)$  of these samples, since in single-carrier-type materials this is normally associated with the charge-carrier density. In HTS's

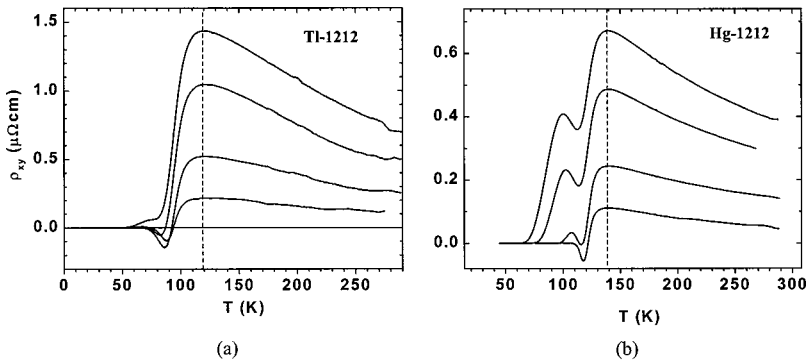


FIG. 2. Hall resistivities for samples (a) TI (1) and (b) Hg (1) for applied magnetic fields 1, 2, 4, and 5.5 T. Dashed lines indicate temperature ( $T_{peak}$ ) at which the characteristic peak occurs.

TABLE II. Comparison of Hall angle data for 1212 samples. (See text.)

Hg and Tl samples	$T_c$ (K)	Slope (Hg)/slope (Tl)	$[T^*/T_c]$ Tl/ $[T^*/T_c]$ (Hg)
1 and 2	120 and 90	2.1	2.02
2 and 1	118 and 87	1.90	1.9

this association cannot be made without difficulty, because of the anomalous temperature dependence of  $n_H \sim T$  observed for almost all HTS's, which presents conceptual problems. A more reliable gauge of the charge-carrier density for these materials is the Hall angle  $\cot \theta_H$  in light of the Anderson Luttinger-liquid model, Eq. (1), which clearly shows a linear relationship between the slope of  $\cot \theta_H(T^2)$  and charge-carrier density  $n$ . Experiments on YBCO, in which charge-carrier density has been manipulated by adjusting oxygen content, have verified such a relationship.<sup>9–11</sup> A particularly interesting result is one in which Rice and co-workers<sup>10</sup> showed that the slope varies with  $T_c$  in the same way as does the doping level.

To check this possibility with the 1212 species, longitudinal and transverse (Hall) resistivities were measured. Longitudinal resistivity for Tl-1212 sample 1 and Hg-1212 sample 1 at fields of 1, 2, 4, and 5.5 T are shown in Fig. 1, revealing little to no field dependence in the normal state. Hall resistivities for these same samples and fields are shown in Fig. 2, showing the expected peak at temperature  $T_{\text{peak}}$ . (The interesting features seen in the mixed state will be presented in a separate paper.) In particular, the temperature scaling of the inverse Hall mobility  $\mu^{-1} = H \cot \theta_H$  was studied, where  $\cot \theta_H$  is the ratio between longitudinal and transverse resistivities. Toward this end,  $\mu^{-1}$  was plotted normalized to temperature  $T_{\text{peak}}$ , Fig. 3. The choice of  $T_{\text{peak}}$  was made on the basis that this parameter is independent of magnetic field for each sample (Fig. 2), strongly suggesting it to be intrinsic to the material. The normalization has the added advantage

of screening out any effects due to the small variations in effective sample dimensions.

$\mu^{-1}$  was found to display the expected  $T^2$  dependence as seen in almost all HTS's. (The plots for  $\mu^{-1}$  were found to overlap for all magnetic fields.) Quite noticeably the plots for Hg-1212 samples are steeper than those for Tl-1212 samples. The actual slopes are summarized in the table in Fig. 3. The slopes for the higher- $T_c$  samples, Hg (1) and Tl (2) differ by a factor of about 2—see Table II. This factor is lower for the lower- $T_c$  samples Hg (2) and Tl (1). For the more optimally doped samples, then, this suggests that their charge-carrier densities differ by approximately a factor of 2.

As a means of providing independent confirmation of this factor of 2 difference in the charge-carrier densities, we utilize a result found in a recent study by Jin and Ott,<sup>9</sup> which shows evidence of a correlation between charge-carrier density and the so-called characteristic temperature  $T^*$  below which  $\cot \theta_H(T^2)$  starts to systematically deviate from  $\sim T^2$  dependence. Since the optimum  $T_c$  for the two 1212 species differs by 30 K, our specific interest is in the reduced values  $T^*/T_{\text{peak}}$ . These values are summarized in the table in Fig. 3 and compared in Table II. The reduced  $T^*$  values differ by a factor of about 2, consistent with the result from the slopes, with a slightly smaller ratio for lower- $T_c$  samples. These results strongly suggest the possibility, then, that *the cation exchange causes a doubling of charge-carrier density which, in turn, induces the 30-K shift in  $T_c$ , as effected by the consequent redistribution of oxygen in the unit cell due to the different valences of Hg and Tl cations.* In addition, this challenges the popular notion that HTS's have a universal optimal doping level, since the distribution of Cu ions in the primitive cells for both species is identical.

It should be noted that there is a small distribution in the slopes that is consistent with the variation in  $T_c$ . The lower- $T_c$  Tl-1212 sample has a *higher slope* than that for the higher- $T_c$  Tl-1212 sample, which is contrary to those of the Hg-1212 samples. This makes sense if Hg-1212 samples are *underdoped*, thus requiring more charge-carrier density to achieve higher  $T_c$ , while the Tl-1212 samples are *overdoped*, thus requiring less charge-carrier density to achieve higher  $T_c$ .

#### IV. CONCLUSION

Comparing the slopes of the normal-state  $\cot \theta_H$  as a function of temperature implies, by Eq. (1), that the 30-K shift in  $T_c$  as a result of substituting the Tl cation in Tl-1212 to produce Hg-1212 is due to a doubling in charge-carrier density most likely because of the consequent change in oxygen concentration and distribution.

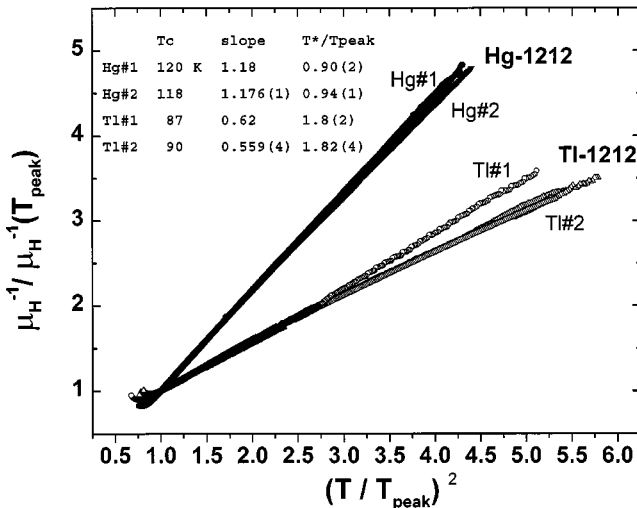


FIG. 3. Normalized inverse Hall mobility for “1212” species versus square of reduced temperature. Table lists values of slopes and ratios  $T^*/T_{\text{peak}}$  (see text and Fig. 2).

These unique “1212” species, due to their high isomorphism, present an alternative method of studying the relationship between doping level  $n$  and critical temperature  $T_c$ . Unlike most other studies in  $T_c(n)$  in which oxygen levels are varied for the one species—and, which, in turn, could alter the crystal structure—this comparative approach maintains constant structural anisotropy, which makes it possible to isolate the role of *electronic* structure in the variation of  $T_c$ . Further studies using this approach could provide a useful, alternative probe into the mechanism of high- $T_c$  superconductivity.

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<sup>1</sup>For a review, see N. P. Ong, in *Physical Properties of High Temperature Superconductors*, edited by D. M. Ginsburg (World Scientific, Singapore, 1990), Vol. II, p. 459.

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