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Hall coefficient for oriented $Tl_2Ba_2CaCu_2O_{8+\delta}$ thin films

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Measurements of the Hall coefficient and resistivity for highly oriented $Tl_2Ba_2CaCu_2O_{8+\delta}$ thin films are reported. The temperature dependence of $\cot\Theta_H$, where Θ_H is the normal-state Hall angle, for a single-phase (2:2:1:2) film sample and for other Tl-based phases is found to be linear in T^2. This behavior is in agreement with recent predictions based on Anderson's spinon-holon model, but it is surprisingly general since it still holds for samples in which the resistivity does not follow Anderson's predicted linear behavior and in which superconductivity is partially or completely suppressed.

The normal-state electron-transport properties of the high-temperature superconducting oxides present an anomaly.[1,2] None of the transport coefficients has been more puzzling than the Hall effect.[3] The family of Tl-based high-T_c oxides with its high number of stoichiometric phases $Tl_mBa_2Ca_{n-1}Cu_nO_{2n+m+2}$ (m=1,2; n=1,2,3,4), most of which are superconducting, offers a unique system for study of normal-state transport. In particular, measurements of the anisotropic transport coefficients (in the *ab* plane and along the *c* axis) for the different phases and their derivatives that can be produced by selective site doping would be very useful. Single-crystal Hall measurements have been reported, however, only for the (2:2:0:1) phase and its variations produced by doping with excess oxygen.[4] We report Hall coefficient and resistivity measurements for thin-film (2:2:1:2) samples that are highly oriented with the *c* axis normal to the substrate. Consequently, the measurements are expected to correspond to transport in the *ab* plane of a single-crystal sample.

The thin films have been grown using an amorphous BaCaCu alloy precursor which has been thermally oxidized and into which Tl has been diffused at high temperature to grow the oriented (2:2:1:2) films. This technique for production of oriented films has been described in detail previously.[5–7] X-ray diffraction scans for two films, *A* and *B*, are shown in Fig. 1. Both show a high degree of orientation with the *c* axis aligned normal to the single-crystal MgO (100) substrate. Based on the x-ray diffraction patterns, film *B* is essentially single phase (2:2:1:2); whereas a small amount of (2:2:2:3) phase can be readily identified in the x-ray pattern for *A*.

A four-terminal method was used for the resistance measurements while the Hall coefficient was measured with a three-terminal configuration which allowed electrical alignment of the Hall probes by balancing the potentiometer across the two Hall electrodes on one side to null the voltage when the field was zero. Measurements were taken at fixed temperatures as a function of field up to 6 T. The thicknesses of the films were measured with an alpha-step profilometer. The films were rough; consequently, the average value of thickness was used. Further uncertainties in the thickness measurement may arise because of a nonconducting Tl_2O_3 layer on the top surface which might result from the Tl diffusion process and a possible dead layer on the bottom surface from reaction with the substrate at the diffusion temperature. Contacts were made by depositing silver pads onto the film and scratching the film to leave the electrode pattern shown in the inset of Fig. 3.

The resistivity for two samples (*B* and *A*) is shown as a function of temperature in Fig. 2. Values for T_c (R =0) are 106 and 105 K, respectively. The magnitude of room-temperature resistivity for *B* is comparable to that reported for a single-crystal (2:2:1:2) phase sample,[8] but the T = 0 intercept of this film is much less than that of the single-crystal sample. This value of room-temperature resistivity is much greater, both for the film and the single crystal, than values around 250 $\mu\Omega$ cm reported for good single-crystal Bi (2:2:1:2) samples.[9] The deviation from a linear temperature dependence of ρ is apparent below approximately 200 K. This deviation may be due to fluctuations or inhomogeneity broadening or a combination of both. Extrapolation of the linear portion to T = 0 gives a value of ρ_0 = 56 $\mu\Omega$ cm and ρ_0 = 60 $\mu\Omega$ cm for *B* and *A*, respectively, although the linear region for *A* is not as well delineated. There is no indication of the higher T_c (2:2:2:3) phase in ρ (T) for either sample, but there is an unusual temperature dependence of R_H (T) and field dependence of the Hall voltage for sample *A* which reflects the presence of this second phase.

Values of R_H^{-1} for the two samples are shown as a function of temperature in Fig. 3. The common linear variation in temperature is found for sample *B* , but there is a minimum near 125 K for sample *A*, i.e., near the T_c

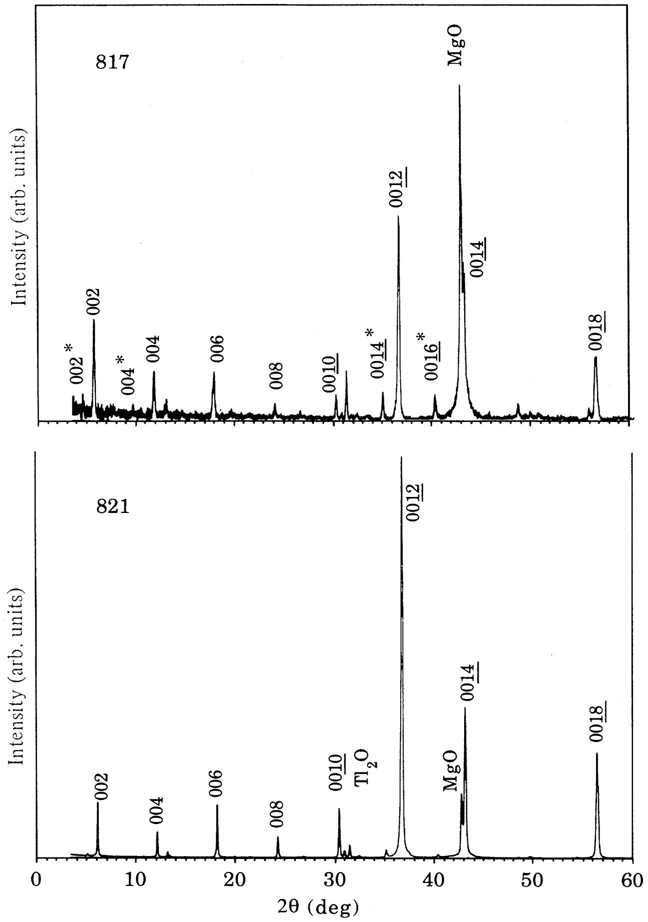

FIG. 1. X-ray diffraction scans for two nominally (2:2:1:2) phase thin films. Lines identified with the (2:2:2:3) phase are indicated by an asterisk. Sample *A* is the upper scan, and sample *B* is the lower one.

value for the (2:2:2:3) phase. We have observed similar minima only for samples of Bi- and Tl-based oxides that were known to be multiphase. With the three-terminal configuration of the Hall contacts (inset to Fig. 3) these R_H measurements will be more sensitive to inclusions of the different phase since any small amount of that phase experiencing a superconducting transition within the region bounded by the two contacts along one side would produce a current redistribution and a change in the electrical balance for the three-contact probe as the region became superconducting. This behavior produced a symmetric contribution to the Hall voltage as a function of field for *A* and other multiphase samples, that is only observed at temperatures between the transition temperature of the (2:2:2:3) phase and that of the (2:2:1:2) phase, along with the usual antisymmetric term associated with the Hall coefficient. This unusual field dependence of the Hall voltage has provided a much more sensitive indication of the presence of a small amount of a higher-T_c second phase than standard x-ray, resistivity or thermopower measurements in many of our samples, and should be checked in Hall effect measurements for these complicated crystals, particularly for samples which exhibit nonlinearity of R_H^{-1} with T.

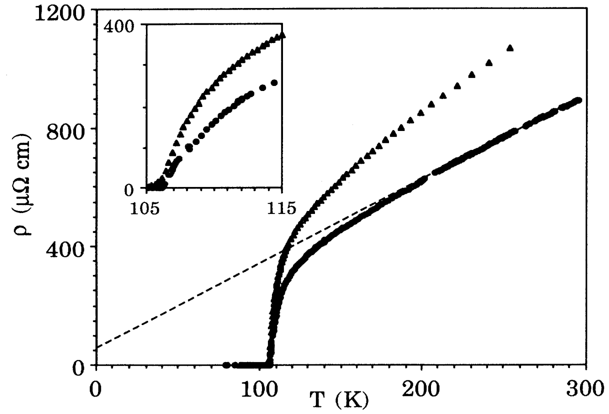

FIG. 2. Resistivity as a function of temperature for the same films: Solid triangles, sample *A*; solid circles, sample *B*.

A linear increase in R_H^{-1} was predicted by Mott[10] in his spin bipolaron picture. This is consistent with our data in Fig. 3, particularly for sample *B*. Although such a linear increase in R_H^{-1} has been seen in other high-T_c superconductors, in Tl 2:2:0:1 and 1:2:1:2 materials a minimum in R_H^{-1} is seen[11,12] near 100 K. Even in these materials, however, a linear increase in R_H^{-1} is a reasonable description of the data above about 150 K.

Anderson[13] has recently proposed an expression for the Hall angle measured in the Cu-O planes for the high-T_c superconducting oxides,

$$\cot\Theta_H = \frac{\rho_{xx}}{R_H B_z} = \alpha T^2 + C \tag{1}$$

in the context of his spinon-holon model by distinguishing the scattering rate τ_{tr}^{-1} , which governs the resistivity, from the tranverse (Hall) relaxation rate τ_H^{-1} which is de-

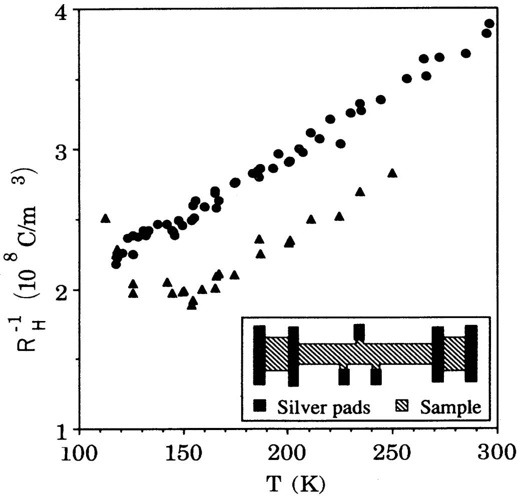

FIG. 3. The reciprocal of the Hall coefficient as a function of temperature for the same two films: Solid triangles, sample *A*; solid circles, sample *B*. The pattern of the electrodes and film is shown in the inset.

termined by scattering of the spinons only. He proposes that the T^2 term arises from spinon-spinon scattering, and that α is a constant which depends on the bandwidth of these excitations. The constant term C is attributed to scattering of the spinons from magnetic impurities in the Cu-O planes. Measurements of the Hall angle for zinc-doped Y-Ba-Cu-O single crystals[14] are in excellent agreement with these predictions. The coefficient α was found to be essentially independent of the concentration of zinc while the constant C increased linearly with the zinc concentration. The extrapolated value of the normal state resistivity at $T = 0$, ρ_0, was observed to increase linearly with zinc content as T_c decreased. Chien, Wang, and Ong[14] suggest that this simple dependence of Θ_H on temperature and doping level appears to rule out the usual multiband models which assume that the transport and the transverse relaxation rates are linearly related.

To test this idea in the Tl-based high-T_c superconductors, data for the single-phase sample (B) is plotted. Also plotted are data from Kubo and co-workers on oxygen doped (2201) sintered[11] and single-crystal[4] samples and oxygen doped $\mathrm{TlSr_2CaCu_2O_{7+\delta}}$ sintered[12] samples. The results are quite interesting; all of the samples exhibit an approximately linear dependence of $\cot\Theta_H$ on T^2. For the sintered samples, the tensor nature of the Hall coefficient precludes a direct theoretical comparison with the coefficient α of Eq. (1), but an analysis in terms of the spinon bandwidth, W_s, as described by Chien, Wang, and Ong[14] can be made for the single-crystal (2:2:0:1) sample and the oriented (2:2:1:2) film. The data of Fig. 4 for these two samples would indicate values of 1280 and 880 K for W_s for the (2:2:0:1) and (2:2:1:2) samples, respectively, following Chien, Wang, and Ong's assumption of one electron/Cu atom. These values are consistent with the value 830 K estimated by Chien, Wang, and Ong[14] for Zn-doped Y-Ba-Cu-O single crystals in agreement with Anderson's estimate. For the sintered $\mathrm{Tl_2Ba_2Cu\ O_{6+\delta}}$ samples, there is a systematic decrease in the intercept C in Eq. (1) with increasing oxygen doping, while for the $\mathrm{TlSr_2CaCu_2O_{7+\delta}}$ samples there is no significant change in C with oxygen content. There appears to be less change in the residual resistivity of the (1:2:1:2) samples than of the (2:2:0:1) sample with oxygen doping,[15] and the corresponding difference in the change of the intercept C is consistent with Anderson's model. We also note that the intercepts C for the single-crystal (2:2:0:1) sample and our oriented (2:2:1:2) film are smaller than for any of the sintered samples plotted in Fig. 4, which is consistent in Anderson's model with less disorder scattering in the crystal and oriented film. For both the (2:2:0:1) and Sr-substituted (1:2:1:2) superconductors, the oxygen-rich samples have the lower T_c and lower ρ (more overdoped); however, the oxygen content is more than stoichiometric (δ positive) for (2:2:0:1), but less than stoichiometric (δ negative) for (1:2:1:2).

The agreement of measurements of the Hall angle on a wide variety of samples with Anderson's theory is impressive. Exceptions have been reported for 124 and 247 Y-Ba-Cu-O polycrystalline samples and for $\mathrm{Nd_{1.85}Ce_{0.15}CuO_{4+\delta}}$ single crystals,[16] but the most intriguing aspect is why exceptions to Anderson's prediction fail to occur for the overdoped samples in which superconductivity is absent. The fact that Eq. (1) still describes the data well for these cases casts doubt on whether the agreement with Eq. (1) is directly related to the superconductivity. It was pointed out[2] that in fact Eq. (1) is also the behavior expected for the case of a conventional metallic material with R_H constant and a T^2 term in the resistivity, as seen, for example, in disordered metals or in metals with scattering of electrons by spin fluctuations. Thus the generality of the T^2 behavior of $\cot\Theta_H$ may not be so surprising. What is surprising is that there is no significant difference in the slope of the T^2 law of the Tl (2:2:0:1) sintered samples[12] for superconducting samples (T_c up to 81 K) and nonsuperconducting samples (see Fig. 4). Although data for these sintered samples cannot be compared directly with the theoretical values of α which relate to the Hall angle in the Cu-O planes, this does suggest a mechanism for the T^2 behavior of $\cot\Theta_H$ which is not dependent on a specific model for the superconductivity, nor on the temperature dependence of the normal-state resistivity, which does change as T_c is suppressed.

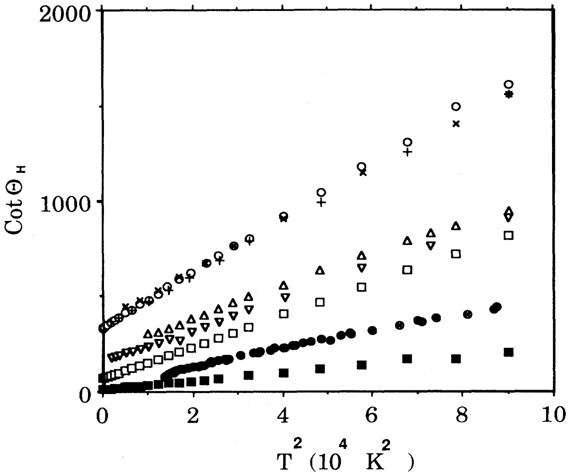

FIG. 4. Values of $\cot\Theta_H = \rho xx/R_H B_z$ as a function of the square of the temperature calculated from values of R_H and ρ with $B_z = 8$ T for sample A (2:2:1:2), several $\mathrm{Tl_2Ba_2CuO_{6+\delta}}$ sintered samples with different values of δ taken from Kubo *et al.* (Ref. 12) and a single-crystal sample taken from Manako *et al.* (Ref. 4), and three $\mathrm{TlSr_2CaCu_2O_{7+\delta}}$ sintered samples taken from Kubo *et al.* (Ref. 12). For thin-film (2:2:1:2) sample solid circles; for $\mathrm{Tl_2Ba_2CuO_{6+\delta}}$, triangles ($\delta = 0.01$), inverted triangles ($\delta = 0.05$), and squares ($\delta = 0.10$) with open symbols indicating sintered samples and solid indicating single-crystal samples; for $\mathrm{TlSr_2CaCu_2O_{7+\delta}}$, crosses ($\delta = -0.20$), plusses ($\delta = -0.16$), and open circles ($\delta = -0.12$).

Such an alternative interpretation has very recently been put forward by Kubo and Manako[15] who suggest the T^2 dependence of the Hall mobility, μ_H, may be interpreted in terms of $\tau_{\mathrm{tr}}^{-1} \cong \tau_H^{-1} \propto T^2$ with a true temperature-dependent carrier concentration given by R_H^{-1}. This is equivalent to the conventional metallic behavior we described[2] in the overdoped limit, in which R_H^{-1} is approximately constant. For the superconducting case at lower hole densities, however, they postulate that the carrier density increases linearly with temperature owing to the two-dimensional ionic nature of these materials. This unconventional temperature dependence of carrier density reduces the resistivity temperature dependence from T^2 to linear in T. We point out that it could also lead to an increased tendency to localization at low temperatures where the carrier density becomes small, an effect which is sometimes indicated by a nonmetallic increase of resistivity as temperature decreases in underdoped samples.

However, it is not obvious how this model would account for the temperature dependence of thermopower in the Tl-based superconductors. In these materials, the thermopower is approximately linear as a function of temperature, but usually does not tend to zero as $T \rightarrow 0$.[2,17] For an overdoped sample with $T_c < 4$ K in the (2:2:0:1) Tl-based phase,[17] however, the thermopower S agrees well with the expected Mott behavior, $S \alpha T$ (i.e., with an essentially zero $T = 0$ intercept), for metallic diffusion thermopower. As the doping level decreases towards the hole concentration for maximum T_c, the thermopower remains approximately linear but is shifted upwards so that it extrapolates to positive values as $T \rightarrow 0$, and in fact becomes positive just above T_c.

In general, a changing carrier concentration is expected to lead to a nonlinear thermopower[18] rather than to a linear thermopower with an offset at $T \rightarrow 0$. This is evident even from the standard Mott expression, where the coefficient of the linear T term depends on the relative energy dependence of the density of states, velocity and relaxation time for the carriers. If the number of carriers (and hence the Fermi energy) change with temperature, the energy dependence of these electronic properties will also change. Hence the thermopower for changing carrier density will in general exhibit curvature as a function of temperature. Thus it is not straightforward to account for the observed linear thermopower in the model of Kubo and Manako[15] in which carrier concentration varies, although it may not be impossible with a multicarrier model.

In conclusion, the first measurement of the Hall coefficient corresponding to the *ab* plane in the (2:2:1:2) phase of Tl-based superconducting oxides has been reported. The temperature dependence of the Hall angle is in good agreement with the predictions by Anderson[13] based on his spinon-holon model. Comparison with other Hall effect measurements for (2:2:0:1) (Refs. 4 and 11) and (1:2:1:2) (Refs. 12) phases also shows similar good agreement in the temperature dependence, even for samples that are near the superconductor-normal metal ($T = 0$) transition which can be achieved by manipulating the oxygen content.

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