RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 38, NUMBER 1 1 JULY 1988

Hall coefficient and oxygen stoichiometry in $YBa_2Cu_3O_{7-\delta}$ ceramics at elevated temperatures

G. S. Grader, P. K. Gallagher, and A. T. Fiory
AT&T Bell Laboratories, Murray Hill, New Jersey 07974
(Received 26 February 1988)

The Hall coefficient and resistivity of polycrystalline ceramic samples of $YBa_2Cu_3O_{7-\delta}$ were measured at elevated temperatures and at various ambient O_2 partial pressures and correlated with separate thermogravimetric measurements of δ. In the region where the oxygen stoichiometry reaches equilibrium with the external O_2, it is shown by isothermal plots that the Hall number density decays exponentially with increasing δ and the effective Hall mobility is weakly dependent on δ. Although transport coefficients are temperature dependent, this result lends support to the picture that oxygen doping in the cuprate acts mainly to modulate the density of hole carriers.

I. INTRODUCTION

Electrical transport in superconducting $YBa_2Cu_3O_{7-\delta}$ exhibits strong anisotropy, as evidenced by epitaxial films and crystals which have higher conductivity in the *a-b* plane,[1,2] and depends sensitively on the oxygen stoichiometry parameter δ.[3,4] Data on ceramic samples give linear temperature dependences for both the resistivity ρ and the Hall number density $n_H = 1/eR_H$, an anomaly that remains open to various theoretical explanations.[5-10] Changes as a function of δ provide important insight into the dependence of transport on oxygen doping, which was previously studied by quenching,[3,4] getter annealing,[11] and *in situ* at elevated temperatures.[12,13] In thermally quenched samples, where a partial loss of oxygen is frozen in, both the conductivity σ and $1/eR_H$ decrease systematically with δ, together with a depression of the superconducting transition temperature T_c.[3,4] Qualitatively, the effect of oxygen stoichiometry is to dope $YBa_2Cu_3O_{7-\delta}$ with hole carriers. The *a-b* plane transport is expected to dominate the electrical measurements on polycrystalline samples.[2,13] For low-temperature annealing methods, the extra oxygen vacancies become ordered,[14,15] particularly distinctive being the $T_c = 60$ K phase. The ordered oxygen-deficient phases are revealed as a modulated structure in the δ dependence of the transport coefficients.[11] This recent finding illustrates the complexity associated with accessing the doping effect on transport when the distribution of the extra oxygen vacancies is not random.

In this work we aim to circumvent some of this difficulty through a study of polycrystalline samples at temperatures that are sufficiently high so that δ is determined by the external O_2 partial pressure P_{O_2} in the ambient.[16,17] For temperatures above about 300 °C at high P_{O_2} and 400 °C at low P_{O_2}, the exchange rate and oxygen diffusivity are large enough for equilibrium to be reached. Under such conditions the oxygen vacancies are also disordered.[18] We find that at fixed temperature the Hall number density $1/eR_H$ is an exponentially decreasing function of δ and that effective Hall mobility $\mu_H = R_H\sigma$ remains fairly constant with δ. Rather than a critical δ_c associated with the metallic to nonmetallic transition, there is instead a continuous transition characterized by a decay-rate parameter δ_0. The isothermal analysis is motivated by the pronounced temperature dependence of all transport parameters.

II. EXPERIMENTAL PROCEDURE

The $YBa_2Cu_3O_7$ samples for this work were fabricated in the form of a ceramic tape following the procedure described previously.[19] Prior to firing, the flexible precursor composite material was cut into cross-shaped samples and Au leads attached at the edges of the arms with Au refractory cement. The samples were placed on a bed of $YBa_2Cu_3O_7$ granules and heated at a rate of 100 °C h^{-1} in O_2 to a sintering temperature of 975 °C, held there for 6 h, and cooled at 200 °C h^{-1}. Samples were finally annealed at 400 °C for 12 h to maximize the oxygen content. Finished samples have 150-μm thickness, ~1-cm overall width, ~5-μm grain size, about 5% porosity, $T_c = 92$ K, and $\rho(295\text{ K}) = 0.8 \pm 0.2$ mΩ cm. Specific contact resistances were about 50 $\mu\Omega\,\text{cm}^2$ using this method, and remain stable over the 20–550 °C temperature range. Contacts, which were applied after firing the ceramic using silver cement,[13] were found to be less reliable, degrading with time at elevated temperatures, particularly at low O_2 pressure. Low contact resistance and low electrical noise from mechanical contact fluctuations are required for accurate Hall measurements. Transport measurements were made according to van der Pauw's method using a gas-flow oven inserted into a rotatable permanent magnet at $H = 0.15$ T. The O_2 partial fractions were fixed at 1, 0.21, 0.01, 0.001, and 0.00005, obtained from O_2-N_2 mixtures which were chemically scrubbed to remove hydrocarbons, H_2O, and CO_2.

The temperature and P_{O_2} range permits a $0.03 < \delta < 0.6$ variation in oxygen stoichiometry, over which the results were reversible and the stresses associated with intercollation did not degrade the sample or the contacts. The $\delta(P_{O_2}, T)$ function was obtained from thermogravimetric analysis of similarly treated samples[17] and in several cases samples were sacrificed for hydrogen-

reduction analyses. Equilibration times up to 24 h were allowed prior to measuring σ and R_H, depending on P_{O_2} and T.

III. RESULTS AND DISCUSSION

In principle, single crystals are preferable to polycrystalline samples. As shown theoretically by Xia and Stroud,[20] a measurement of R_H for polycrystals gives essentially the a-b plane component multiplied by a correction factor which reduces to $\frac{4}{5}$ in the simple one-band model. However, in attempting electrical measurements on single crystals,[21] we discovered that oxygen stoichiometry may not reach equilibrium on account of the much slower O_2 exchange kinetics. This can be explained by scaling oxygen intercollation-rate data on ceramics quadratically with grain or crystal width in the a-b plane.[22,23] Hence, there is a kinetic barrier temperature T_K, which is function of P_{O_2}, crystal dimensions, and wait time. In a pure O_2 ambient, allowing several hours of equilibration, $T_K \lesssim 300\,^\circ$C for many ceramics, while for 1-mm crystals $T_K \gtrsim 550\,^\circ$C. In the case of films, one naturally has to be concerned with substrate interactions.[24]

Our results for the electrical resistance are similar to previous data[12,13] where it was shown that dependences on temperature and δ may be separated into two terms: $\rho(T,\delta)=\alpha T+\rho_0\delta/(\delta_c-\delta)$, where $\delta=\delta(P_{O_2},T)$ and $\delta_c \approx 0.85$. Some variation in the room-temperature sample resistivity was found among several sample batches, even though preparation conditions were similar. Lower resistivity samples generally give smaller Hall coefficients. Although the tape process produces randomly oriented grains, as determined by x-ray diffraction, part of this variability may be due to the platelet shape of the grains, which implies that a simple effective-medium correction factor between ρ_{ab} and the measured ρ is not always exactly 2. Another consideration is grain size and the effect of increasing oxygen deficiency with crystallite size, because of the kinetics discussed above. Concerned that the latter is the more significant criterion, we selected samples with the lowest resistivity, about 0.7 mΩcm at room temperature.

One cannot rule out that part of the temperature dependence in R_H and ρ that is observed below T_K, a region where exchange with the ambient O_2 is probably too slow to be consequential, may be a consequence of reordering of the remaining oxygen deficiency or to macroscopic oxygen diffusion within the sample. Appreciation of this possibility is our primary motivation for focusing on the region above T_K. Figure 1 shows the effective Hall number density $n_H=1/eR_H$ as a function of temperature for various constant P_{O_2}. The reversible regions, temperatures above our estimate of T_K, are shown by solid curves. The equilibrium parts of the isobars, shown by dashed curves, were taken after cooling below T_K. The magnitude of $1/eR_H$ is larger than found in some previous work and in some of our other samples, which we associate with the lower resistivity of this sample. Our electrical measurements show that oxygen exchange essentially ceases below $T_K=290\,^\circ$C for $P_{O_2}=1$ atm and below $\sim 400\,^\circ$C for $P_{O_2} \lesssim 0.1$ atm. This is shown as a dotted curve in Fig. 1,

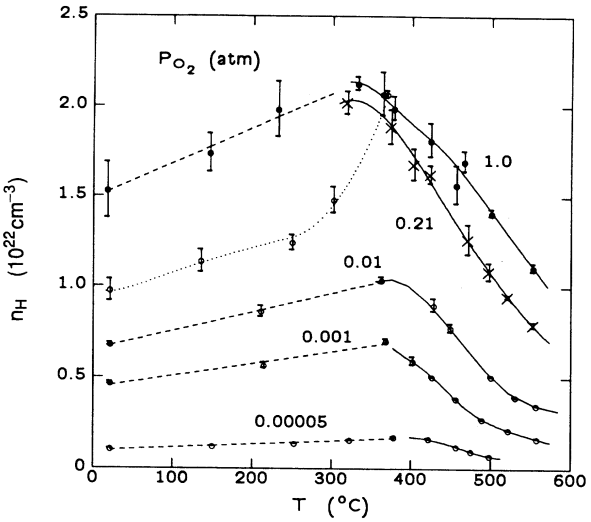

FIG. 1. Temperature dependence of the Hall effect in $YBa_2Cu_3O_{7-\delta}$ ceramic at various ambient P_{O_2}. Solid curves connect points in the equilibrium region; dashed curves, below the kinetic barrier limit; and dotted curve, an inhomogeneous-quenched sample, as discussed in the text.

where the sample was intentionally prepared with an inhomogeneous oxygen stoichiometry by heating to 550 °C at $P_{O_2}=0.01$ atm, cooling, and switching to pure O_2 at about 500 °C. This produces oxygen-deficient cores within many of the grains. The region below T_K falls intermediately between the $P_{O_2}=1.0$ and 0.01 points, and rejoins the $P_{O_2}=1.0$ curve above T_K.

Data taken below room temperature show more clearly the linear temperature dependence of $1/eR_H$, which leads to a quadratic temperature dependence of the effective mobility μ_H in the region $T<T_K$.[9,10] This strong temperature dependence is presently not understood from two-dimensional band theory,[25] although compensation has been mentioned.[9,10] However, these observations are remarkably similar to the extraordinary Hall effect associated with skew scattering by local magnetic moments.[26]

Desorption of oxygen and an increase in δ above T_K causes $1/eR_H$ to peak above T_K, decreasing at high temperature. To isolate the δ dependence from the pressure and temperature dependences, we constructed isothermal plots of Hall number and mobility, as shown in Figs. 2 and 3. For δ we have taken thermogravity data, which are similarly affected by nonequilibrium for points at $T \lesssim T_K$. Hence, the lowest temperature isotherms, which are approaching T_K, may be influenced by nonequilibrium. On a plot with linear scales, $1/eR_H$ curves continuously as a function of δ. This is unlike the conductivity, which after correcting for the αT term in ρ, was found previously to approach zero at a critical $\delta_c \approx 0.85$. Hence, we find that $1/eR_H$ apparently does not extrapolate to zero at a critical point in a similar manner. This result comes about because the conductivity at a given δ is less temperature sensitive than $1/eR_H$. The data in Fig. 2 were fitted by the expression $n_H=n_0e^{-\delta/\delta_0}$. The prefactor $n_0 \approx 2\times10^{22}$ cm^{-3} does not vary significantly with temperature. However, δ_0 depends on temperature as shown in Fig. 4.

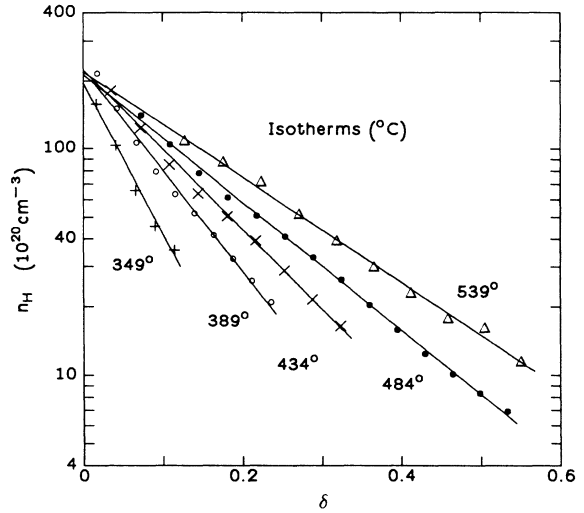

FIG. 2. Isotherms giving the δ dependence of the effective Hall number density and exponential fits.

Considering the hypothesis that the decrease in conductivity is due to disorder associated with the excess oxygen vacancies and appealing to predictions of the scaling theory of localization, one should expect no renormalization of the Hall coefficient.[27] A similar theoretical result was found for corrections due to electron-electron Coulomb interactions.[28] These theoretical predictions were confirmed by experiments on low-carrier-density indium oxide superconductors.[29] This is to be contrasted with data on doped semiconductors, where both the conductivity and the Hall number density drop to zero at a critical point with separate power-law exponents.[30] The semiconductor experiment is probably an exceptional case not relevant to understanding the present experiment because in $YBa_2Cu_3O_{7-\delta}$ the carrier density is orders of magnitude larger, Coulomb interactions are much stronger, and the insulating phase is antiferromagnetic.[31] Thus we take that there is no strong renormalization of $1/eR_H$ due to disorder, for a given dopant density.

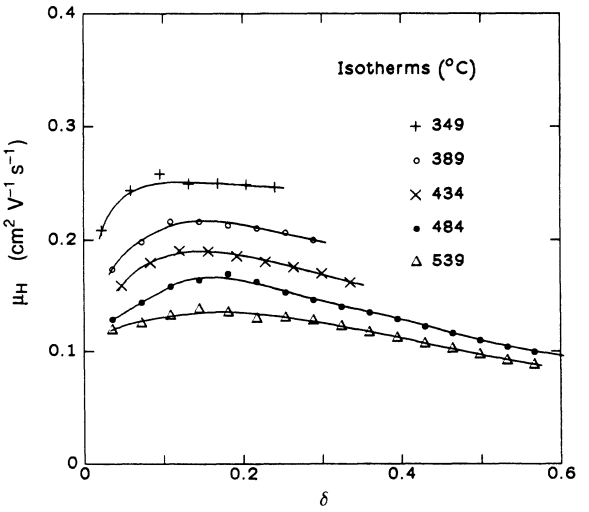

FIG. 3. Isotherms giving the δ dependence of the effective Hall mobility.

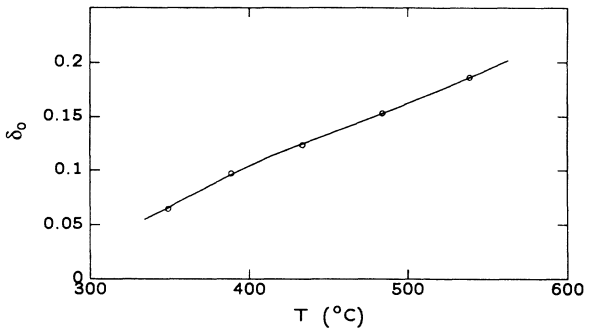

FIG. 4. The exponential decay constant used to fit Hall data of Fig. 2.

Although band effects may alter the details, we will argue that $1/R_H$ is essentially proportional to the hole carrier density, because it gives a consistent interpretation of the data in Figs. 2 and 3. The isothermal curves in Fig. 3 show that the effective mobility is almost constant. Absence of a decrease in μ_H with oxygen removal implies weak lattice-defect scattering compared to phonon scattering and little change in the effective mass. Hence, the data of Fig. 2 can be interpreted as a depletion of the hole density as oxygen is removed. This conclusion is supported by recent theoretical total-energy calculations and photoemission experiments which indicate that the Hubbard potential U is large at both Cu and O sites, that the oxygen valence is, therefore, closer to -1 than -2, and that the oxygen, therefore, controls the electronic doping.[32]

Recent nuclear quadrupole resonance relaxation data, $T \leq 300$ K, suggest that the carrier density at Cu sites is depleted at $\delta \approx 0.3$.[33] This is qualitatively consistent with the exponential dependence observed. Although our presentation separates the temperature dependence from the stoichiometry dependence, it is important to recognize that the orthorhombicity of the sample cannot be kept constant as δ is varied. Moreover, the variation of orthorhombicity with δ is temperature dependent.[13,18]

IV. CONCLUSIONS

Ceramic samples offer the ability of studying a broad range of uniform oxygen stoichiometry $\delta(P_{O_2}, T)$ in a region above the oxygen-exchange kinetic-barrier limit. Plotting our Hall effect data as isotherms, rather than as isobars, reveals an exponential dependence of the effective hole carrier density on oxygen content, as $n_H = n_0 e^{-\delta/\delta_0}$. That the effective mobility remains constant with δ, to a good approximation, implies that the presence of oxygen in the central Cu-O chains of $YBa_2Cu_3O_{7-\delta}$ dopes the crystal with hole carriers, and that the perturbation by oxygen disorder is comparatively minor.

ACKNOWLEDGMENTS

It is a pleasure to acknowledge stimulating conversations with R. N. Bhatt, D. W. Johnson, Jr., S. Martin, H. M. O'Bryan, W. W. Rhodes, L. F. Schneemeyer, and J. V. Waszczak.

[1]Y. Enomoto, T. Murakami, M. Suzuki, and K. Moriwaki, Jpn. J. Appl. Phys. Lett. **26**, L1248 (1987).

[2]S. W. Tozer, A. W. Kleinsasser, T. Penney, D. Kaiser, and F. Holtzberg, Phys. Rev. Lett. **59**, 1768 (1987).

[3]S. Uchida, S. Tajima, H. Takagi, K. Kishio, T. Hasegawa, K. Kitazawa, K. Fueki, and S. Tanaka, Jpn. J. Appl. Phys. **26**, Supl. 3, 1105 (1987).

[4]Z. Z. Wang, J. Clayhold, N. P. Ong, J. M. Tarascon, L. H. Greene, W. R. McKinnon, and G. W. Hull, Phys. Rev. B **36**, 7222 (1987).

[5]M. W. Shafer, T. Penney, and B. L. Olson in *Novel Superconductivity,* edited by S. A. Wolf and V. Z. Kresin (Plenum, New York, 1987), p. 771; T. Penney, M. W. Shafer, B. L. Olson, and T. S. Plaskett, Adv. Ceram. Mater. **2**, 577 (1987).

[6]S.-W. Cheong, S. E. Brown, Z. Fisk, R. S. Kwok, J. D. Thompson, E. Zirngieble, G. Gruner, D. E. Peterson, G. L. Wells, R. B. Schwarz, and J. R. Cooper, Phys. Rev. B **36**, 3913 (1987).

[7]U. Gottwick, R. Held, G. Sparn, F. Steglich, H. Rietschel, D. Ewert, B. Renker, W. Bauhofer, S. von Molnar, M. Wilhelm, and H. E. Hoenig, Europhys. Lett. **4**, 1183 (1987).

[8]H.-M. Duan, L. Lu, X.-M. Wang, S.-Y. Lin, and D.-L. Zhang, Solid State Commun. **64**, 489 (1987).

[9]P. Chaudhari, R. T. Collins, P. Freitas, R. J. Gambino, J. R. Kirtley, R. H. Koch, R. P. Laibowitz, F. K. LeGoues, T. R. McGuire, T. Penney, Z. Schlessinger, A. P. Segmuller, S. Foner, and E. J. McNiff, Jr., Phys. Rev. B **36**, 8903 (1987).

[10]A. Davidson, A. Palevski, M. J. Brady, and P. Santhanam (unpublished).

[11]R. J. Cava, B. Batlogg, C. H. Chen, E. A. Rietman, S. M. Zahurak, and D. Werder, Nature **329**, 423 (1987).

[12]G. S. Grader, P. K. Gallagher, and E. M. Gyorgy, Appl. Phys. Lett. **51**, 1115 (1987).

[13]A. T. Fiory, M. Gurvitch, R. J. Cava, and G. P. Espinosa, Phys. Rev. B **36**, 7262 (1987).

[14]C. Chaillout, M. A. Alario-Franco, J. J. Capponi, J. Chenavas, J. L. Hodeau, and M. Marezio, Phys. Rev. B **36**, 7118 (1987).

[15]R. M. Fleming, L. F. Schneemeyer, P. K. Gallagher, B. Batlogg, L. W. Rupp, and J. V. Waszczak, Phys. Rev. B **37**, 7920 (1988).

[16]K. Kishio, J. Shimoyama, T. Hasegawa, K. Kitazawa, and K. Fueki, Jpn. J. Appl. Phys. Lett. **26**, L1228 (1987).

[17]P. K. Gallagher, H. M. O'Bryan, S. A. Sunshine, and D. W. Murphy, Mater. Res. Bull. **22**, 995 (1987).

[18]J. D. Jorgensen, M. A. Beno, D. G. Hinks, L. Soderholm, K. J. Volin, R. L. Hitterman, J. D. Grace, I. K. Schuller, C. U. Segre, K. Zhang, and M. S. Kleefisch, Phys. Rev. B **36**, 3608 (1987).

[19]D. W. Johnson, Jr., E. M. Gyorgy, W. W. Rhodes, R. J. Cava, L. C. Feldman, and R. B. van Dover, Adv. Ceram. Mat. **2**, 364 (1987).

[20]T.-K. Xia and D. Stroud, Phys. Rev. B **37**, 118 (1988).

[21]For crystal preparation, see L. F. Schneemeyer, J. V. Waszczak, T. Siegrist, R. B. van Dover, B. Batlogg, R. J. Cava, and D. W. Murphy, Nature **328**, 601 (1987).

[22]H. M. O'Bryan and P. K. Gallagher, Adv. Ceram. Mater. **2**, 640 (1987).

[23]G. S. Grader, P. K. Gallagher, J. Thompson, and M. Gurvitch, Appl. Phys. A **45**, 179 (1988).

[24]M. Gurvitch and A. T. Fiory, Appl. Phys. Lett. **51**, 1027 (1987).

[25]P. B. Allen, W. E. Pickett, and H. Krakauer, Phys. Rev. B **37**, 7482 (1988).

[26]A. Fert and A. Friederich, Phys. Rev. B **13**, 397 (1976); S. P. McAlister and C. M. Hurd, Phys. Rev. Lett. **37**, 1017 (1976).

[27]B. Shapiro and E. Abrahams, Phys. Rev. B **24**, 4025 (1981).

[28]B. L. Altshuler, D. Khmel'nitzkii, A. I. Larkin, and P. A. Lee, Phys. Rev. B **22**, 5142 (1980).

[29]A. T. Fiory and A. F. Hebard, Phys. Rev. Lett. **52**, 2057 (1984).

[30]S. B. Field and T. F. Rosenbaum, Phys. Rev. Lett. **55**, 522 (1985).

[31]N. Nishida, H. Miyatake, D. Shimada, S. Okuma, M. Ishikawa, T. Takabatake, Y. Nakazawa, Y. Kuno, R. Keitel, J. H. Brewer, T. M. Riseman, D. L. Williams, Y. Watanabe, T. Yamazaki, K. Nishiyama, K. Nagamine, E. J. Ansaldo, and E. Torikai, Jpn. J. Appl. Phys. Lett. **26**, L1856 (1987).

[32]M. Schluter, M. S. Hybertsen, and N. E. Christensen, Physica B (to be published).

[33]W. W. Warren, R. E. Walstedt, G. F. Brennert, G. P. Espinosa, and J. P. Remeika, Phys. Rev. Lett. **59**, 1860 (1987); and (unpublished).