PHYSICAL REVIEW B VOLUME 44, NUMBER 21 1 DECEMBER 1991-I

Effect of oxygen depletion on the transport properties of $YBa_2Cu_3O_{7-\delta}$

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(Received 25 June 1991)

We report measurements of the resistivity (ρ), thermoelectric power (TEP), and Hall coefficient (R_H) of sintered $YBa_2Cu_3O_{7-\delta}$ for a range of δ values and for temperatures up to 300 K. As δ is increased, T_c increases slightly, reaching a maximum for δ close to 0.1, and the TEP changes sign from negative to positive, while R_H is positive for all values of δ. At low values of δ there is a marked increase in the fluctuation conductivity, which we have analyzed in terms of Aslamazov-Larkin fluctuations to determine the out-of-plane correlation length $\xi_\perp(0)$. A corresponding analysis of specific-heat data enables us to deduce the in-plane correlation length as well. We discuss the strong dependence of the Hall number on temperature and δ.

As part of a wider study on several families of high-T_c oxides, including high-resolution specific-heat measurements, we report here resistivity (ρ), thermoelectric power (TEP), and Hall coefficient (R_H) data for sintered bars of $YBa_2Cu_3O_{7-\delta}$ as a function of oxygen content δ. Although transport studies on single crystals give more information, it is more difficult to control their stoichiometry and to oxygenate them fully, while for sintered pellets the transport properties do seem to be dominated by the highly conducting *ab* planes.

The sample was prepared from CuO, Y_2O_3, and $BaCO_3$ by solid-state reaction, and after being ground and sintered several times, it was divided into two pellets. The larger one, which was used for specific heat and Hall measurements, had a density of 5.1 g/cm^3, while that used for ρ and TEP measurements had a density of 5.5 g/cm^3 and an average grain size of 20–30 μm. High-precision electron-probe microanalysis (EPMA) showed that cation stoichiometry was 1:2:3 within the experimental accuracy ($\pm 2\%$) and that variations from grain to grain were undetectable ($< \pm 0.5\%$). δ was varied by quenching into liquid nitrogen for various combinations of anneal temperature and oxygen partial pressure,[1] and its value was deduced from the weight change of the larger pellet. Resistivity measurements were made using a four-probe ac method at 77 Hz with current densities ≈ 0.1 $A\,cm^{-2}$. Thermoelectric power measurements were made using the usual steady-state technique, with a small reversible temperature difference of 0.4–1 K. Hall measurements were conducted by rotating the sample by 180° in a magnetic field of 7 T, and checks for a linear response were made for at least two temperatures in fields of 1–7 T.

In Fig. 1 are shown $\rho(T)$ data for the same bar of $YBa_2Cu_3O_{7-\delta}$ at different oxygen depletions δ. For $\delta=0$, the extrapolated residual resistivity ρ_{res} is close to zero, a property that we believe to be indicative of a high-purity sample.[2,3] As δ is increased, the temperature region of downward curvature in $\rho(T)$ above T_c grows rapidly, and ρ_{res} increases linearly with δ (up to $\delta=0.4$) with only a slight increase in the slope $d\rho/dT$; these changes are reversible. T_c (defined as the temperature at which the TEP is 1% of its value just above the transition) initially rises slightly for low values of δ (see also Fig. 4), and we observe a double transition in $\rho(T)$ which disappears for values of $\delta > 0.05$.[4] This feature has been consistently observed for those samples with $\rho_{res} \approx 0$, and also has been detected in the TEP. The curvature above T_c is usually attributed to the presence of superconducting fluctuations,[5] which are more pronounced in high-T_c oxides because of their relatively low normal-state conductivity and the low values of coherence length. These fluctuations were analyzed as follows. A linear background was obtained by fitting $\rho(T)$ at higher temperatures to the expression $\rho(T)=AT+B$ (A and B constants). Good fits at the level of the scatter of the data ($\pm 0.1\%$) were obtained in the temperature interval 180–280 K, except for $\delta=0$, where the interval was 140–190 K. Deviations from

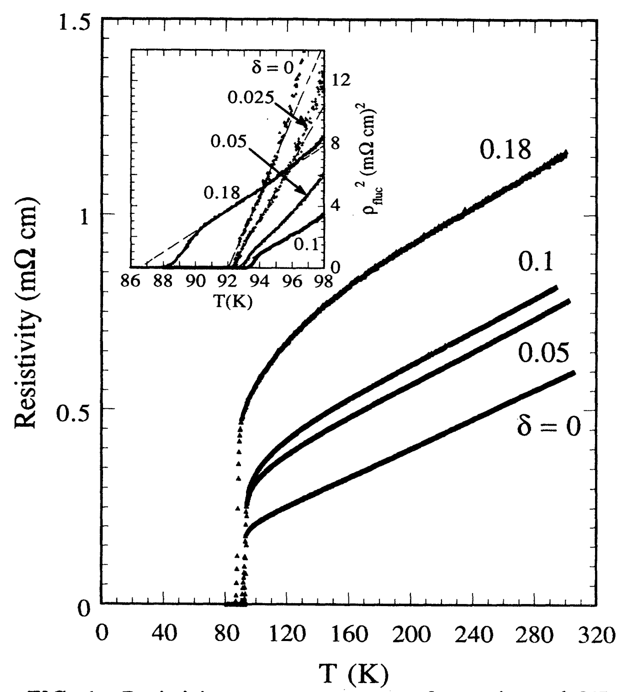

FIG. 1. Resistivity ρ vs temperature for a sintered $YBa_2Cu_3O_{7-\delta}$ sample at low values of δ. The inset shows fluctuation resistivity squared ($1/\sigma'^2$) vs temperature.

this fitted line at lower temperatures were then attributed to the extra conductivity σ' arising from superconducting fluctuations. This procedure is only justified if $\sigma' \approx 0$ above 200 K, for example, because of the argument used by Freitas *et al.*,[5] in which a wavelength cutoff is introduced to discount those short wavelength fluctuations that do not obey the "slow spatial variation" requirement of the Ginzburg-Landau theory. In the three-dimensional (3D) limit, the standard Aslamazov-Larkin contribution to σ' is[6]

$$\sigma' = \frac{e^2}{32\hbar\xi_\perp(0)} \left[\frac{T_c}{T - T_c} \right]^{1/2}, \qquad (1)$$

where $\xi_\perp(0)$ is the coherence length perpendicular to the CuO_2 layers and where the in-plane coherence length ξ_{ab} has been assumed to be isotropic. In Fig. 1 (inset) $1/\sigma'^2$ has been plotted versus T for each value of δ. Extrapolation of the curves to $1/\sigma'^2 = 0$, gives a divergence temperature $T_c^* = 92.5 \pm 0.5$ K except for $\delta = 0.18$. The increased fluctuation contribution with oxygen depletion is illustrated by the strong dependence of the slope of the lines in Fig. 1 (inset) on δ. The values of $\xi_\perp(0)$ were obtained by making a correction of a factor of 4, corresponding to the difference between the room temperature conductivity of a single crystal ($\rho_{aa} = 150\ \mu\Omega\,\mathrm{cm}$) (Ref. 7) and our ceramic samples.[2] $\xi_\perp(0)$ was found to be 2.8, 2.3, 1.8, 1.4, and 1.5 Å for $\delta = 0$, 0.025, 0.05, 0.1, and 0.18, respectively. If the anomalous Maki-Thompson term[6] is included in the 3D fits with the pair-breaking parameter $(T_{c0} - T_c)/T_{c0} \approx 0.1$, then the values of $\xi_\perp$ are increased by approximately a factor of 2. Complementary information is obtained from a fluctuation analysis of the specific heat,[8] where the slope of $(1/\Delta C)^2$ vs T corresponds to the coherence volume. Using the coherence volumes so deduced, as well as the values of $\xi_\perp$ given above, we obtain values for the average in-plane coherence lengths ξ_{ab} ranging from 11 Å for $\delta = 0$ to 9.9 Å for $\delta = 0.1$. Thus it appears that the strong enhancement of fluctuation effects at low oxygen depletion is largely due to the decoupling of the copper oxide planes and the associated reduction in $\xi_\perp$. This is consistent with the increase in conductivity anisotropy σ_{ab}/σ_c of single crystals of $YBa_2Cu_3O_{7-\delta}$ as oxygen is removed.[9] We note that cobalt doping produces similar effects.[3]

Figure 2 shows the corresponding TEP data. For all samples which are both well oxygenated, and have $\rho_{res} \approx 0$, the TEP is found to be negative. However, several batches from different sources (mainly commercial) were found to have $\rho_{res} > 0.2\ \mathrm{m}\Omega\,\mathrm{cm}$ and a positive TEP, even after extended oxygen annealing treatments. We believe that at least for low δ, the sign and the magnitude of the room-temperature TEP is a sensitive empirical guide to the degree of order and purity of the CuO chains in $YBa_2Cu_3O_{7-\delta}$. The TEP remains small (less than 5 μV/K) for samples with $T_c \approx 90$ K, and actually changes sign for δ corresponding to the maximum in T_c. The standard interpretation of this behavior is that there is a negative contribution from the CuO chains, which at $\delta = 0$ dominates the positive contribution from carriers in the CuO_2 planes. This is supported by single-crystal work which gives a negative TEP for the b direction.[10] The negative contribution is then progressively suppressed as oxygen is removed from the chains. However, we have recently found a similar sign change in two other systems[11] [the septenary compound $Y_xCa_{1-x}Sr_2(Tl_{0.5}Pb_{0.5})Cu_2O_7$ (Ref. 12) and $Bi_2Sr_2CaCu_2O_{8+x}$], which suggests that there is a universal cause linking the sign change of the TEP with the maximum in T_c; namely that it is a property of the CuO_2 planes themselves at particular doping levels rather than a specific property associated with the CuO chains in $YBa_2Cu_3O_{7-\delta}$.

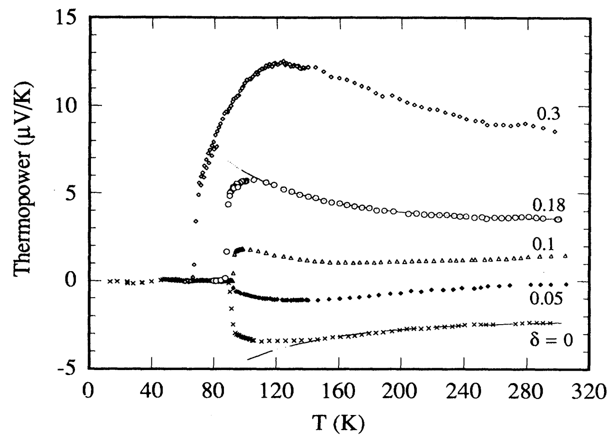

FIG. 2. Thermoelectric power vs temperature for $YBa_2Cu_3O_{7-\delta}$ at various values of δ. For $\delta = 0$ and 0.18 fits to the law $CT + D/T$ are also shown.

Recently two interpretations of the nonmetallic (nonlinear) T dependence of the TEP in high-T_c oxides have been proposed. In one interpretation, the data were fitted to a law of the form $CT + D/T$, where the first term corresponds to the normal carrier diffusion TEP and the second to the phonon drag TEP.[13] We find that good fits of this form are obtained for $\delta = 0$ with C and D negative and for $\delta = 0.18$ with C and D positive (see Fig. 2). However our data are not consistent with the freezing out of umklapp processes[13] for holes because the deviations from the above law are of opposite sign for $\delta = 0$ and 0.18, and furthermore the fits are not good for intermediate values of δ. In another interpretation, the diffusion TEP is enhanced by the effect of an anomalously large electron-phonon coupling which introduces a $1/T$ dependence.[14] There is experimental evidence for a factor of 2 enhancement of the electronic specific-heat coefficient which is fairly constant for low values of δ.[8] On the other hand, we cannot rule out other scenarios involving magnetic excitations. The influence of superconducting fluctuations on the TEP (Ref. 15) should be taken into account when making detailed fits.

Figure 3 shows plots of Hall number n_H vs T. In contrast to the TEP, n_H remains positive for all δ. Near $\delta = 0$, n_H vs T flattens off above 250 K. A similar effect was recently reported for single crystals of $YBa_2Cu_3O_{7-\delta}$ by Chien *et al.*[16] For $\delta > 0.05$, this behavior disappears, and n_H falls linearly with T although it does not extrapolate through the origin. Detectable deviations from linearity occur above T_c at temperatures corresponding to the onset of superconducting fluctuations in the resistivity

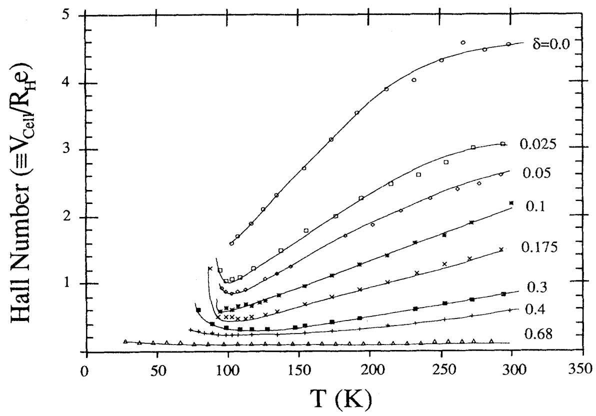

FIG. 3. Hall number vs temperature for $YBa_2Cu_3O_{7-\delta}$ at various values of δ. The lines are a guide to the eye.

data in Fig. 1. Following Chien *et al.*,[16] we have also looked for a $1/T^3$ dependence of the Hall conductivity $\sigma_H = R_H/\rho^2$ or a $1/T^2$ dependence of the Hall angle R_H/ρ. Both laws are reasonably good for $\delta = 0$; however, for higher δ (up to 0.4), the latter law gives a better fit to the data outside the fluctuation region. Higher precision measurements up to 400 K for $\delta = 0$ show a change in exponent from 3 to 2.5 in σ_H and from 2 to 1.5 in the Hall angle above ~ 250 K.

In Fig. 4 we have plotted T_c and room-temperature TEP, as well as normalized values of conductivity, $d\rho/dT$, Hall conductivity, and Hall number as a function of δ.

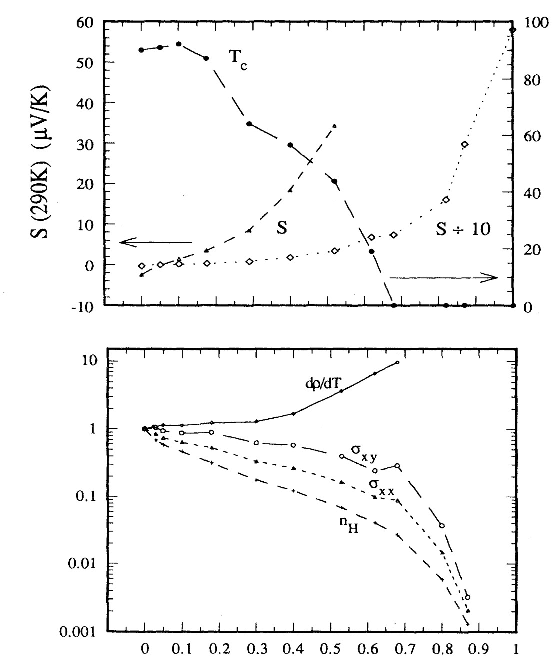

FIG. 4. T_c and room-temperature values of thermoelectric power (S), and normalized values of Hall number, conductivity (σ_{xx}), σ_{xy}, and $d\rho/dT$ plotted as a function of δ for $YBa_2Cu_3O_{7-\delta}$.

Our quenched samples show the plateau in T_c at 60 K reported by other workers[17] with superconductivity disappearing between $\delta = 0.62$ and 0.68. Some aging effects have been observed for quenched samples, most probably due to ordering in the CuO chains;[18] these decrease $\rho(T)$ and increase n_H by up to 20% but have little effect on temperature dependences.

As δ increases above 0.18, the TEP increases strongly and is large, positive, and nonmetallic, even for those samples with T_c as high as 60 K. In the region where the TEP is large, it should be possible to correlate the values of the TEP with the carrier concentration in the CuO_2 planes as determined by bond valence sum analyses.[19] The semilogarithmic plot of n_H vs δ shows three regions. For $\delta < 0.1$ n_H falls very sharply with δ, then over more than one decade of n_H, it depends exponentially on δ. An exponential dependence was found in cobalt-substituted $YBa_2Cu_3O_{7-\delta}$ by Clayhold *et al.*,[20] and we have also found a similar behavior of n_H vs x in $Y_xCa_{1-x}Sr_2(Tl_{0.5}Pb_{0.5})Cu_2O_7$.[21] Finally in the nonsuperconducting region above $\delta = 0.68$, n_H and σ_{xx} both fall very sharply. The room-temperature values of n_H vary from 4.5 holes per unit cell at $\delta = 0$ to 0.3 holes at $\delta = 0.53$. Simple electron counting arguments lead to much smaller values and a weaker dependence on δ. Recent Hall data on oxygen-depleted $YBa_2Cu_3O_{7-\delta}$ crystals[22] (with field parallel to the c axis and current flow in the ab plane) show the same behavior with δ (except near $\delta = 0$ where sintered samples are more reliable), although values of R_H are a factor of 2 larger than ours. This confirms the empirical observation that R_H for sintered samples corresponds to the ab-plane component of the Hall tensor for a single crystal.[23] According to a simple argument,[24] the conductivity tensor of a polycrystalline sample is given by the average of the three principal components for a single crystal. For $YBa_2Cu_3O_{7-\delta}$ $\sigma_{cc} \ll \sigma_{aa}, \sigma_{bb}$, and experimentally R_H is of order $1/ne$ for all magnetic field and current orientations,[23] so it follows that $\bar{\sigma} \approx (\sigma_{aa} + \sigma_{bb})/3$ and $\bar{R}_H = 2R_H^{ab}/3$ (if $\sigma_{aa} = \sigma_{bb}$) or $\bar{R}_H \approx 0.6 R_H^{ab}$ (if $2\sigma_{aa} = \sigma_{bb}$ as found by Friedmann *et al.*[7] for $\delta = 0$). Averaging over the various possible magnetic-field orientations will give a further reduction in R_H, by a factor of 2, for a sintered sample. Our value $R_H = 0.5 R_H^{ab}$ is thus consistent with this argument. However, the effect of porosity[2] on R_H still needs clarification. As shown in Fig. 4 the Hall conductivity σ_{xy} as well as $d\rho/dT$ are relatively independent of δ for $\delta \lesssim 0.2$. This should be checked for single crystals, so that the possibility of grain boundary contributions to ρ_{res} can be eliminated.

Within the simple two-band picture mentioned previously, the carriers on the chains in $YBa_2Cu_3O_{7-\delta}$ propagate in one dimension, and their contribution to σ_{xy} $(= \rho_{xy}\sigma_{xx}\sigma_{yy})$ is negligible due to the small value of σ_{yy}. (Actually for a quasi-1D system $\rho_{xy} \approx 1/ne$ for a constant relaxation time,[25] and is zero for a constant mean-free-path model.[26]) Therefore they can contribute to the current without contributing to the Hall voltage and can enhance the value of n_H. This mechanism may be relevant between $\delta = 0$ and 0.1. As δ increases, the conductivity of the chains should decrease, and R_H should become more and more a property of 2D CuO_2 planes. In the 2D limit σ_{xy} is directly related[26] to an area in the "mean-free-path plane" (l_x, l_y) generated as the electron wave vector traces out the 2D Fermi surface in **k** space. A Fermi surface with large flat portions [such as that calculated for the CuO_2 planes in $YBa_2Cu_3O_{7-\delta}$ (Ref. 27)] will give anomalous behavior since σ_{xy} will be strongly influenced by the values of l_x and l_y on the curved regions, while σ_{xx} will be dominated by the larger flat regions. However, the unusual behavior of the TEP and the enhancement of both the magnetic susceptibility and the specific heat lead us to believe that renormalization effects causing an energy dependent effective mass and mean free path play an important role.

In conclusion, we note that measurements on other high-T_c oxide systems indicate that the change in the sign of the TEP and the exponential fall in Hall number on doping reported here for $YBa_2Cu_3O_{7-\delta}$ occur more generally and are, therefore, associated with the CuO_2 planes rather than the specific "plane-chain" structure of $YBa_2Cu_3O_{7-\delta}$. Removal of oxygen from $YBa_2Cu_3O_{7-\delta}$ strongly enhances fluctuation effects above T_c, because disruption of the CuO chains decouples the CuO_2 planes and, thereby, reduces the values of the perpendicular coherence length $\xi_\perp$.

We are grateful to W. Y. Liang and J. L. Tallon for several useful discussions, to J. S. Edmends for setting up the Hall apparatus, to P. A. Freeman for preparing the high-quality $YBa_2Cu_3O_7$ sample, and to A. P. Mackenzie for EPMA measurements.

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[1]Annealing conditions were as follows: 12 h in flowing oxygen at temperatures 370, 420, 470, 520, and 570 °C for δ values of 0, 0.025, 0.05, 0.1, and 0.18, respectively; 12 h in flowing 2% oxygen in nitrogen at 510, 550, 600, 650, and 680 °C for δ values of 0.29, 0.4, 0.5, 0.62, and 0.68, respectively; 12 h in flowing 0.2% oxygen in nitrogen at 650 and 705 °C for δ values of 0.81 and 0.87, respectively; vacuum annealing at 650 °C for 5 h for $\delta=1$.

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