Anomalous Transport Properties in Superconducting $Nd_{1.85}Ce_{0.15}CuO_{4\pm\delta}$

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(Received 4 February 1994)

We report a comprehensive study of the in-plane transport properties of $Nd_{2-x}Ce_xCuO_{4\pm\delta}$ epitaxial thin films and crystals by both increasing and decreasing δ with Ce content fixed at $x \approx 0.15$. We find a remarkable correlation between the appearance of superconductivity and (1) a positive magnetoresistance in the normal state, (2) a positive contribution to the otherwise negative Hall coefficient, and (3) an anomalously large Nernst effect. These results strongly suggest that both holes and electrons participate in the charge transport for the superconducting phase of $Nd_{2-x}Ce_xCuO_{4\pm\delta}$.

PACS numbers: 74.76.Bz, 72.15.Eb, 72.15.Gd, 74.25.Fy

In most high-T_c cuprates, such as $La_{2-x}Sr_xCuO_4$ and $YBa_2Cu_3O_7$, the charge carriers are doped holes. On the other hand, in $Nd_{2-x}Ce_xCuO_{4-\delta}$ (NCCO), where superconductivity is induced by substituting Nd^{3+} with Ce^{4+}, the CuO_2 planes are believed to be doped with electrons [1]. The "electron-doped" character of NCCO gives a strong constraint on the possible mechanisms for high-temperature superconductivity in copper oxides [2,3]. Recently this system has attracted much more interest because of its possible simple BCS s-wave pairing in the superconducting state [4], in contrast to d-wave behavior proposed for hole doped high-T_c cuprates [5]. However, questions still remain concerning the nature of the charge carriers in the superconducting phase of NCCO. For instance, both a negative and a positive Hall coefficient R_H have been reported [6–8], and in some crystals the thermopower S has a positive (holelike) sign opposite to that of the negative (electronlike) Hall coefficient [9]. To account for these experimental results, a two-band model was proposed by some of these authors [7,9] suggesting the existence of holes in NCCO. This could have important implications for the theory of high-T_c superconductivity, but this model has not been considered seriously since it was based on only a few isolated experiments. There are also some theories which propose that there must be hole carriers in NCCO to explain the occurrence of superconductivity [10]. Lacking so far is a systematic and reliable experimental study of transport properties on well characterized NCCO materials. This is largely due to the difficulty of studying this system with varying Ce concentrations because the oxygen content varies for different Ce dopings. Closely related to this is the long-standing puzzle of why bulk superconductivity occurs in $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$ only after an oxygen reduction. This suggests that the role played by oxygen is far more complicated in NCCO than that in the hole-doped cuprates.

Here we report the first comprehensive study of the in-plane transport properties of epitaxial $Nd_{1.85}Ce_{0.15}CuO_{4\pm\delta}$ thin films and crystals. We fix the Ce content at 0.15 and vary the oxygen content from well below to well above the optimum concentration for maximum T_c. We find that, in the normal state of the superconducting phase of NCCO, the Hall angle $\tan\theta_H$ $(= \sigma_H/\sigma)$ obtained from the Hall effect and resistivity measurements is much smaller than $\tan\theta_T$ $(= E_N/E_S)$ obtained from the Nernst and Seebeck effects, a result strikingly incompatible with a simple one conduction band model which would give $\tan\theta_T = \tan\theta_H$. This Hall angle discrepancy is much reduced in an oxygenated nonsuperconducting sample. Together with our measurements of other transport properties, these data provide compelling evidence for the existence of both electron and hole carriers in NCCO. The highly mobile doped electrons dominate the transport properties for fully oxygenated samples, and the hole carriers increasingly dominate as oxygen is removed. More importantly, the samples that are superconducting lie near the threshold where hole conduction starts to dominate, which implies that holes play an important role in this electron-doped superconductor.

High quality NCCO films were deposited [11] by pulse laser deposition in an N_2O environment. The as-made films are superconducting with $T_c \approx 21$ K and transition width $\Delta T_c \leq 1$ K as determined by ac susceptibility and resistivity. The oxygen content was then changed by annealing the films either in vacuum (1×10^{-5} torr) or in partial oxygen pressure (~400 torr) at 450–600 °C but the exact oxygen content at each annealing stage cannot be determined. Both oxygenation and deoxygenation processes were found to be fully reversible and the films retain the T'-214 structure as revealed by x-ray diffraction, transmission electron microscope cross sectional images, and electron diffraction techniques. For the present study, two nearly identical films with a thickness about 2000 Å were used. Sample SN1 is used for the oxygenated regime (adding oxygen) and SN2 for deoxygenated states (removing oxygen). The use of two films with optimum T_c for the two regimes allows us to more easily locate the sample in the T_c vs δ phase diagram, because it is difficult to precisely control the oxygen content of a particular sample.

Figure 1(a) shows the T dependence of the in-plane resistivity ρ for film SN1 annealed in oxygen at the same temperature for different lengths of time: curves a to f correspond to increasing oxygenation with $t = 15$ min

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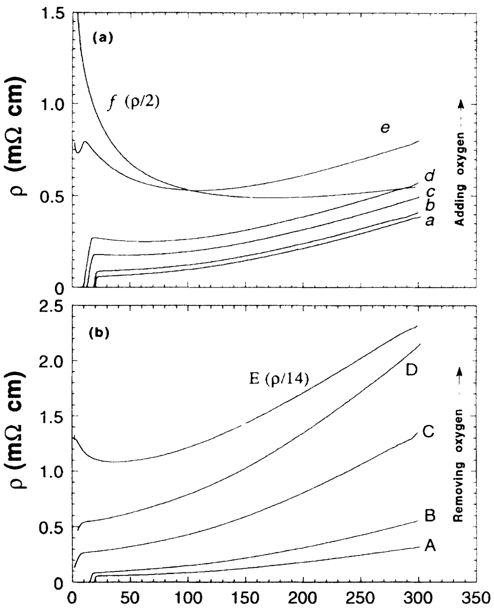

FIG. 1. In-plane resistivity of $Nd_{1.85}Ce_{0.15}CuO_{4\pm\delta}$ vs T for (a) film SN1 annealed in oxygen and (b) film SN2 annealed in vacuum. Curves a to f (A to D) represent different annealing stages in oxygenation (deoxygenation) process.

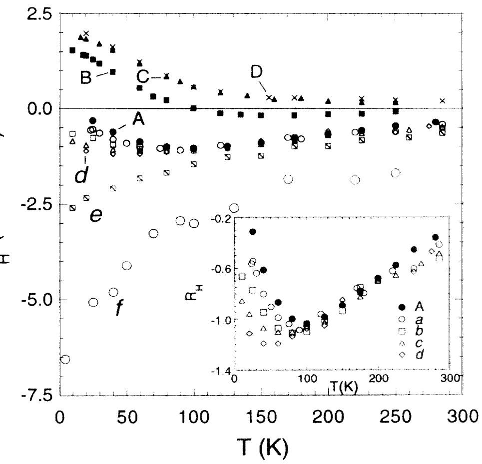

FIG. 2. T dependence of the Hall coefficient of $Nd_{1.85}Ce_{0.15}CuO_{4\pm\delta}$ films with varying oxygen content. Labels f to D are the same as used in Fig. 1. Inset: A close view of R_H for superconducting samples (d to A).

for curve f. As the oxygen is gradually added to sample SN1 (curve a), which has the maximum T_c ($\approx$ 21.3 K), T_c is suppressed and the normal state resistivity increases monotonically. In the range that the sample is superconducting, the most significant effect of adding oxygen is to increase the residual resistivity with $d\rho/dT$ unaffected for T above ~80 K. This indicates an increase of the impurity scattering by excess oxygen. The excess oxygen also localizes the charge carriers as an upturn in ρ develops at low T with increasing oxygen content. The magnetoresistance (MR) in the upturn regime also shows a crossover from positive to negative as the magnetic field is increased, a behavior typically caused by the competition between superconductivity and localization.

Figure 1(b) shows ρ versus T for film SN2 annealed in vacuum at the same temperature for different lengths of time: curves A to E refer to increasing deoxygenation with $t = 36$ minutes for curve E. In contrast to annealing in oxygen, both the magnitude and the slope of ρ changes rapidly as the oxygen content is reduced, indicating that the density of mobile carriers is strongly modified. While T_c decreases as oxygen is gradually removed, the resistivity goes up quickly and the sample becomes insulating without any detectable structural transition before it decomposes.

Shown in Fig. 2 is the T dependence of the in-plane Hall coefficient R_H for the same films in Fig. 1. The magnitude of R_H decreases with decreasing oxygen content (from f to D) and changes sign from negative to positive. We can see three distinct ranges in which R_H is affected by the oxygen doping quite differently. In range I (curves f to d), the magnitude of R_H decreases rapidly and its strong T dependence at low T is suppressed as oxygen is removed. As soon as superconductivity occurs, that is, in range II (curves d to A, which are shown more clearly in the inset), an upturn toward positive in R_H starts to develop at low T and the minimum of R_H shifts toward higher temperature. The inset clearly shows that oxygen reduction only affects R_H at $T \leq 100$ K but not above, suggesting that the mobile carrier density is unchanged. This is consistent with Fig. 1(a) in that $d\rho/dT$ does not change in this range. When oxygen is further removed from the sample (range III, curves A to D), deoxygenation changes R_H dramatically even when T_c is only reduced by a few degrees from the maximum T_c (see curve B), and eventually causes the sign change in R_H. Such a behavior has not been reported for NCCO with varying Ce concentration.

In Fig. 3, we plot T_c (determined from the midpoint of the resistivity transition), the magnetoresistance, and the Hall coefficient at 60 K as a function of annealing time in oxygen (left side) and in vacuum (right side). The annealing time is assumed to be proportional to the oxygen content of the sample. As shown in Fig. 3(a), T_c has a maximum at an optimum oxygen doping, in agreement with the behavior observed in all high-T_c cuprates [12]. Also plotted in Fig. 3(a) is ρ(300 K) which has a minimum at the optimum oxygen content for T_c. The increase of ρ with decreasing oxygen content (i.e., increasing electron density) on the deoxygenation side is quite remarkable since in previously reported studies of doping effects in cuprates, including Ce doping in NCCO, the resistivity decreases monotonically with increasing carrier doping. This anomalous behavior of ρ is accompanied by the sign change in R_H as shown in Fig. 3(c). A possible explanation for this behavior is that the electronic structure of NCCO is strongly affected by oxygen doping.

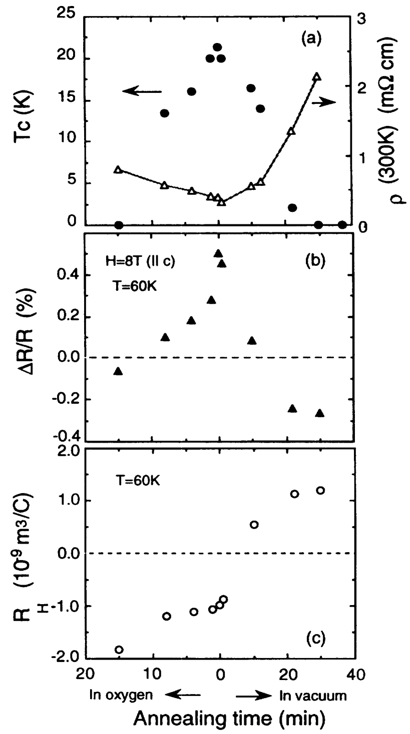

FIG. 3. Variation of (a) superconducting transition temperature T_c and ρ(300 K), (b) magnetoresistance at 60 K and $H = 8$ T, and (c) the Hall coefficient at 60 K with the annealing time in oxygen and vacuum.

An interesting observation is that in the film with $T_c \approx 17$ K (curve B in Fig. 2), which is slightly overdoped from the optimum oxygen content, the normal state R_H changes sign with decreasing temperature. Such a behavior has never been observed in any p-type cuprate and is difficult to understand within a single conduction band model. Some groups observed a similar behavior in some NCCO crystals and thin films [7,8], and it was speculated that the inhomogeneity of the samples might cause such an unusual behavior [8]. The present study indicates that this sign change in R_H with varying temperature is an intrinsic property of NCCO at a particular oxygen doping.

Angle-resolved photoemission revealed that NCCO has a simple Fermi surface [13]. In such materials, the most straightforward way to understand the sign change of R_H with varying temperature is in terms of a two-band conduction. In a general two-band picture with weak magnetic fields, the transport coefficients are given by [14]

$$R_H = (\sigma_1^2 R_{H1} + \sigma_2^2 R_{H2})/\sigma^2, \quad (1)$$

$$\tan\theta_H = (\sigma_{H1} + \sigma_{H2})/\sigma, \quad (2)$$

$$S = (\sigma_1/\sigma)S_1 + (\sigma_2/\sigma)S_2, \quad (3)$$

$$Q = \{Q_1\sigma_1\sigma + Q_2\sigma_2\sigma + (S_1 - S_2)\sigma_1\sigma_2(R_{H1}\sigma_1 - R_{H2}\sigma_2)\}/\sigma^2, \quad (4)$$

where σ_i, σ_{Hi}, and R_{Hi} represent, respectively, the longitudinal, the Hall conductivity elements, and the Hall coefficient of band i and $\sigma = \sigma_1 + \sigma_2$. θ_H is the total Hall angle. S and Q are the Seebeck (i.e., thermopower) and the Nernst coefficients as we describe later. If the electronic structure of NCCO consists of an electronlike band and a holelike band, the sign change of $R_H(T)$ could be interpreted as a competition between these bands if the scattering rate of each band has a different T dependence.

One signature of two-band conduction is a positive magnetoresistance (i.e., the classical MR). For two types of carriers having densities n_1 and n_2 and mobilities μ_1 and μ_2, the transverse MR is given [15] by $\Delta\rho(H)/\rho(0) = [n_1 n_2 \mu_1 \mu_2 (\mu_1 - \mu_2)^2] H^2/(n_1\mu_1 + n_2\mu_2)^2$ which indicates that $\Delta\rho/\rho \propto H^2$. Indeed, we observed a positive MR for all superconducting samples which varies as $\sim H^2$ for $T \geq 60$ K (these temperatures are much higher than T_c so magnetoresistance caused by the suppression of superconducting fluctuations can be neglected). In nonsuperconducting samples, however, the MR is negative. In Fig. 3(b) we plot $\Delta\rho(H)/\rho$ at $T = 60$ K as a function of oxygen doping. Comparing with Fig. 3(a), we see a remarkable correlation between the occurrence of superconductivity and the appearance of a positive MR.

Another evidence for two-band conduction is the small Hall angle measured by the resistivity and the Hall effect as compared to that determined by the Seebeck and Nernst effects. The Nernst voltage, analogous to the Hall effect, arises from diffusion of carriers in a temperature gradient with a perpendicular magnetic field, i.e., $E_N = Q(\partial T/\partial x)H$, Q is the Nernst coefficient which is independent of the sign of the charge carriers [14]. For metals with a single band and an energy dependent relaxation time $\tau(\varepsilon)$, the diffusion thermopower at $T \ll T_F$ is $S = (-\pi^2 k_B^2 T/3e)\{\partial \ln\sigma(\varepsilon)/\partial\varepsilon\}_{\varepsilon=\mu}$, where $\sigma = ne^2\tau/m$ is the conductivity and μ is the Fermi energy. The Nernst coefficient is given by $Q = (\pi^2 k_B^2 T/3m)\{\partial\tau(\varepsilon)/\partial\varepsilon\}_{\varepsilon=\mu}$, where m is the effective mass [15]. The Hall angle $\tan\theta_T$ determined by E_N/E_S $(= HQ/S)$ is thus exactly the same as $\tan\theta_H = \sigma_H/\sigma$. For two-band conduction with electrons and holes, $\tan\theta_H$ becomes small as can be seen from Eq. (2) since σ_{H1} and σ_{H2} have opposite signs. On the other hand, because both electrons and holes drift in the same direction in a temperature gradient, the total thermopower S is reduced and the Nernst coefficient is enhanced leading to a large $\tan\theta_T$ as also can be seen from Eqs. (3) and (4). Therefore, a large discrepancy between $\tan\theta_H$ and $\tan\theta_T$ is expected. Our measurements on superconducting NCCO thin films and crystals with optimum T_c show that the normal state Nernst voltage is proportional to H as expected, but its magnitude is very large, leading to a large Hall angle $\tan\theta_T$ as shown in Fig. 4. Assuming the measured thermopower is due to the diffusion of the charge carriers, we obtain $\tan\theta_T \approx 0.14$ and $\tan\theta_H \approx 0.007$ for the NCCO crystal at 30 K and $H = 4$ T, indicating that $\tan\theta_T \approx 20\tan\theta_H$. Similarly, $\tan\theta_T \approx 30\tan\theta_H$ is obtained for the thin film sample. This anomalously large discrepancy cannot be explained

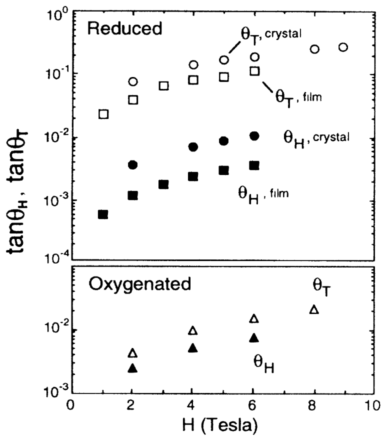

FIG. 4. Magnetic field dependence of the tangent of Hall angle in the normal state ($T = 30$ K) for a reduced ($T_c \approx 24$ K) and an as-grown (i.e., oxygenated, $T_c = 0$) NCCO crystal. Also shown are the data for a reduced NCCO film with $T_c \approx 22$ K.

within a conventional single band model and is most likely caused by a two-band effect. However, we cannot rule out more exotic transport models perhaps based on electron correlation effects. It would be interesting to see if such models could explain all the data that we have presented in this paper.

As evidenced in Figs. 2 and 3, when the oxygen content of NCCO increases, we expect a crossover from a two-band to a single electron band conduction. For oxygenated and nonsuperconducting NCCO crystals, R_H depends monotonically on the temperature and is negative, in agreement with S on the sign of the charge carriers [6,16]. In this case, $\tan\theta_T$ should become comparable with $\tan\theta_H$. As we expected, on an as-grown (i.e., oxygenated) NCCO crystal we obtained $\tan\theta_T \approx 0.008$ at 30 K and $H = 4$ T as compared to $\tan\theta_H \approx 0.005$, also shown in Fig. 4.

We speculate that the holelike band in NCCO may arise from the buckling of the CuO_2 planes in this material as first suggested by Billinge and Egami [17]. This lattice distortion, perhaps due to the removal of oxygen, will affect the electronic states of the narrow oxygen $2p$ bands. Assuming the CuO_2 planes are flat, these bands were shown to lie just below the Fermi level by the local density approximation calculations [18]. Particularly, the p_z band connecting the planar oxygen and the oxygen in the Nd_2O_2 layer is about 0.4 eV below E_F for Ce doping $x \approx 0.15$. The oxygen displacement along the c direction will shorten the distance between these two oxygen atoms and thus tends to raise the energy of the oxygen p_z band through the Fermi level, giving rise to lattice induced hole states.

The implications of this picture are that there exist two electronic subsystems in NCCO. Highly mobile impurity doped electrons coexist with a lattice distortion induced hole band on the CuO_2 planes. Our transport data are essentially consistent with this model and further suggest that this hypothetical hole band is controlled by oxygen doping. Moreover, our magnetotransport measurements clearly indicate that the electronic band structure of NCCO is strongly modified by oxygen doping: from a single electron band in the fully oxygenated regime to two-band conduction in the superconducting phase and then to one holelike band in the over-deoxygenated state. In particular, the occurrence of superconductivity in $Nd_{1.85}Ce_{0.15}CuO_{4+\delta}$ as oxygen is removed from the oxygenated sample is accompanied by the appearance of the hole band. These observations suggest that the holelike states may be crucial for the occurrence of the superconductivity in this n-type material, thus raising a fundamental question about the nature of the charge carriers which undergo the condensation to the superconducting state in NCCO. We believe our present data are important to the resolution of this question and may stimulate further studies on the nature of the charge carriers in the so-called "electron-doped" cuprates.

We gratefully acknowledge G. Deutscher and Paul M. Grant for stimulating discussions. This work was supported by NSF under Grant No. DMR 9209668.

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