In-plane transport properties of single-crystal $R_{2-x}Ce_xCuO_{4-y}$ (R =Nd,Sm)

S. J. Hagen, J. L. Peng, Z. Y. Li, and R. L. Greene*
Center for Superconductivity Research, Department of Physics and Astronomy, University of Maryland, College Park, Maryland 20742-4111
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We have investigated the in-plane transport properties of high-quality crystals of $R_{2-x}Ce_xCuO_{4-y}$ (R=Nd,Sm) prepared over a range of Ce contents x. We find the Hall coefficient R_H is uniformly negative in superconducting (x near 0.15) and underdoped crystals, indicating electron conduction in the CuO_2 planes, and becomes positive at large doping ($x \sim 0.2$). The in-plane resistivity remains metallic over this range and decreases monotonically as x increases, consistent with an increasing carrier density. These data confirm results on ceramic samples and demonstrate that electron doping in the T'-phase superconductors and hole doping in the T-phase systems affect transport in the same way.

The discovery of superconductivity in the "T'-phase" copper oxides $R_{2-x}M_xCuO_{4-y}$ (R =Nd, Sm, Eu, and Pr; M=Ce and Th),[1,2] with $T_c \sim 25$ K for $x \approx 0.15$, raised the possibility that the mechanism for high-T_c superconductivity in the layered copper oxides could be symmetric with respect to hole or electron doping of the CuO_2 planes. While Sr^{2+} doping in $La_{2-x}Sr_xCuO_4$ (for example) introduces hole carriers into the insulating CuO_2 planes, Ce^{4+} doping in $Nd_{2-x}Ce_xCuO_{4-y}$ should introduce electrons into these layers: The two systems show similar superconducting, metallic, and antiferromagnetic behavior[3] as a function of x. If the charge carriers in the two cases actually are of opposite sign, then mechanisms proposed to explain superconductivity in these systems must work equally well for electron or hole carriers. Since this would provide an important constraint on theory, it is essential to determine whether the carriers responsible for superconductivity in the "electron-doped" materials are in fact electronlike.

Hall-effect measurements[1] on ceramic samples of $Nd_{2-x}Ce_xCuO_{4-y}$ with varying x appeared to confirm that the charge carriers were electrons for underdoped and superconducting samples ($x \leq 0.18$) and holes for overdoped (metallic but not superconducting) samples. Also, ceramic superconducting samples (x =0.15) showed negative thermopower.[4] However, x-ray photoemission and absorption data[5,6] have not consistently confirmed or disproved the presence of electron carriers. Wang *et al.*[7] recently presented data on several single crystals of $Nd_{2-x}Ce_xCuO_{4-y}$ ($x \approx 0.15$) showing a positive Hall coefficient near T_c, indicating the presence of hole carriers. From the positive sign and strong temperature dependence of the Hall effect in these samples, Wang *et al.* argued that superconductivity in $Nd_{2-x}Ce_xCuO_{4-y}$ is in fact produced by hole carriers like those in $La_{2-x}Sr_xCuO_4$. However, their data contradict Hall results on ceramic samples[1] and on crystals[8] of $Nd_{1.84}Ce_{0.16}CuO_{4-y}$. We have investigated this problem by measuring the in-plane Hall coefficient $R_H = E_y / j_x B_z$ and the resistivity ρ of single-crystal $Nd_{2-x}Ce_xCuO_{4-y}$ systematically over a range of doping $0.05 \leq x \leq 0.2$. In these high-quality crystals, we find that the Hall coefficient is negative in superconducting samples for $T_c \leq T \leq 300$ K, in contrast to the results of Wang *et al.* At higher doping ($x \sim 0.2$), superconductivity disappears and R_H changes sign, as in ceramic samples and the $La_{2-x}Sr_xCuO_4$ system.[1,9] The magnitudes of both the Hall coefficient and in-plane resistivity decrease monotonically with an increasing x, consistent with increasing carrier concentration.

We grew $R_{2-x}Ce_xCuO_{4-y}$ (R =Nd and Sm) crystals with various dopings x from a CuO-based flux.[10] X-ray diffraction confirmed the crystal structure and orientation (the c axis is perpendicular to the broad faces); transmission electron microscopy and scanning electron microscopy analyses verified that the crystals were single phase with the (uniform) doping x, expected from the starting compositions. Although the as-grown crystals are not superconducting, annealing in an inert atmosphere (such as Ar) for a long period (> 15 h) at high temperature (~ 900 °C) removes oxygen and produces superconductivity at $T_c \approx 23$ K for x near 0.15. Samples with higher and lower doping did not receive this treatment. Further details on the sample preparation are provided in Ref. 10. We were unable to measure the oxygen deficiency of these crystals, but similar annealing conditions typically produce $y \approx 0.03$ in ceramic $R_{2-x}Ce_xCuO_{4-y}$. Magnetization and resistivity data indicate that superconductivity in our $x \sim 0.15$ crystals is probably more complete and more uniform than in crystals used in previous transport studies. In a 5-Oe magnetic field aligned parallel to the CuO_2 planes, the shielding fraction for individual crystals is $\sim 90\%$ and the Meissner fraction is $\geq 20\%$ at T=5 K. The resistive transition at T_c is found to be very sharp, with $\Delta T \approx 0.8$ K (10–90 %). As shown in Fig. 1, flux-expulsion measurements (with $\mathbf{H} \| c$) verify that a single sharp superconducting transition occurs in the bulk at T_c; there is no indication that lower T_c phases are present. [The crystals in Fig. 1 exhibit zero resistance at T=22.2 K (open

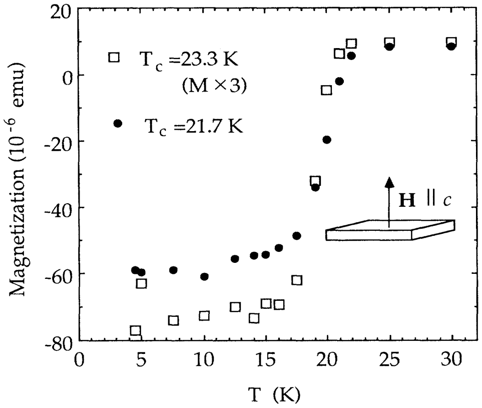

FIG. 1. Field-cooled magnetization vs temperature for two $x \sim 0.15$ crystals, showing a sharp superconducting transition near the resistive T_c's at 23.3 and 21.7 K.

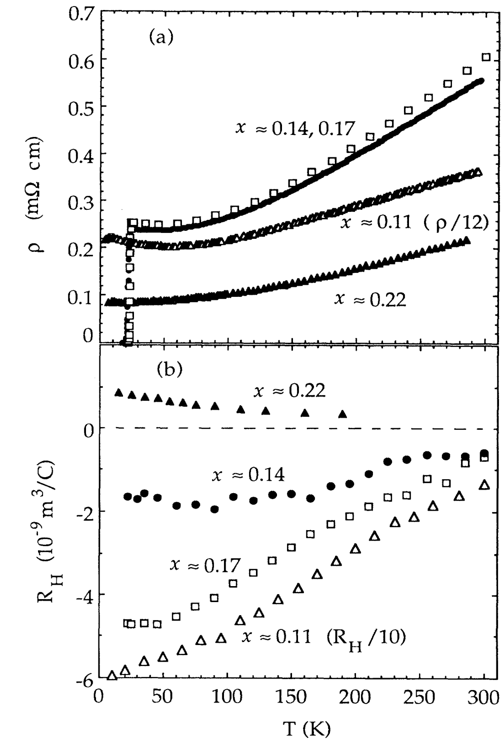

FIG. 2. (a) In-plane resistivity and (b) Hall coefficient vs temperature. Data for $x = 0.14$ and 0.17 are from same crystals as in Fig. 1. Note different scale for $x \approx 0.11$.

squares) and $T = 20.2$ K (solid circles).] Resistive measurements of the critical field $H_{c2}(T)$ versus T (for $\mathbf{H} \| c$) in $x \approx 0.15$ crystals give results similar to those reported in Ref. 18.

We selected several crystals (of typical size $a \times b \times c \sim 2000 \times 1000 \times 25$ μm^3) for measurement of the in-plane resistivity ρ and the Hall coefficient R_H in fields $B \leq 60$ kG ($\mathbf{B} \| c$) and $T \leq 300$ K. The crystals were mounted with indium-alloy contacts in a six-lead configuration for simultaneous measurement of ρ and R_H. We obtained R_H by sweeping the magnetic field from positive to negative values and extracting the slope of the resulting transverse resistance data. In all cases the Hall resistance was linear in field, as expected. Carbon-glass resistor thermometry allowed an accurate temperature measurement in the magnetic field.

Figure 2(a) shows ρ versus T for crystals having $x \approx 0.11$, 0.14, 0.17, and 0.22, where the Ce dopings x were determined to an accuracy of ± 0.02 by wavelength dispersive spectroscopy.[10] Only the two crystals with $x \approx 0.14$ and 0.17 and (same crystals as in Fig. 1) are superconducting above 4 K, but all show metallic conduction with nearly linear resistivity for $T > 100$ K and nearly flat ρ below $T \sim 50$ K. This residual resistivity and the curvature[11] in ρ versus T make ρ of this system more similar to that of conventional metals than to the linear ρ of the p-type cuprate superconductors. We note that the $x \approx 0.11$ sample exhibits largely metallic resistivity despite low doping and the onset of antiferromagnetic ordering[12] below $T \sim 130$ K. This is difficult to understand, since the value of $k_F l = (h/e^2)(CuO_2$ layer separation$)/2\rho \sim 0.7$ (at 100 K) in this sample appears too small for a metallic system. This could indicate that some inhomogeneity of higher x is present; however, it does not affect the clear trend of R_H and ρ with doping or their behavior in the superconducting crystals, which form the focus of this paper.

Figure 2(b) shows the Hall coefficient versus temperature in the same samples. R_H is uniformly negative and clearly temperature dependent in the superconducting and underdoped samples. The magnitude of R_H decreases rapidly as the doping x increases, consistent with an increasing carrier density n. By $x \approx 0.22$, R_H has changed sign to take on a small positive value. In the superconducting crystals, R_H saturates below 50 K: It does not show the $1/T$ behavior seen in the p-type oxide superconductors.[13]

It is interesting to note that the two superconducting crystals have slightly different R_H behavior, even though the resistivities are the same. At low temperature, R_H is more negative for the higher T_c ($T_c = 23.3$ K, $x \approx 0.17$) than the lower T_c ($T_c = 21.7$ K, $x \approx 0.14$) crystal. Given the overall trend in R_H versus doping, this suggests that the lower-T_c sample is slightly overdoped. This may result either from greater Ce content x or from greater oxygen deficiency y; the spectroscopy microprobe does not determine x with sufficient resolution to rule out greater Ce content. Strong sensitivity of R_H to doping, especially for $x \approx 0.14$–0.18, was observed in ceramics by Takagi, Uchida, and Tokura;[1] inhomogeneous doping or oxygen content may therefore account for the positive R_H that some authors[7] reported for crystals showing superconductivity at $T \sim 20$ K.

In a simple free-electron model, the carrier density n would increase linearly with doping if the oxygen deficiency y remained constant. With R_H and ρ inversely proportional to carrier density n, Ce doping would produce a linear increase in the conductivity and the "Hall number" $n_H \equiv$(unit cell volume)/$(e|R_H|)$. However, the

Hall coefficient R_H in metals is not always so simply related to the carrier density; the temperature dependence of R_H in this system already suggests a more subtle connection between n and n_H. Either magnetic ("skew") scattering of charge carriers or the presence of two conduction bands (e.g., both holes and electrons) in the CuO_2 planes would introduce temperature dependence to the Hall data and complicate its interpretation.[14] Although skew scattering in the high-T_c oxides appears unlikely,[7,13] the sign change of R_H at high doping does suggest that both electron and hole bands are present. Nevertheless, the systematic reduction of R_H and ρ with Ce doping, together with the sign of R_H, constitute strong evidence that charge transport in the CuO_2 planes is dominated by electronlike carriers.[15]

However, the observed reduction of R_H and ρ with doping in these crystals is not simply proportional to the Ce content. Figure 3 shows $\log_{10}(\rho)$ and $\log_{10}(n_H)$ versus temperature, where $n_H \propto 1/R_H$ would be the number of carriers per unit cell in a one-band model. Doping reduces ρ and increases n_H uniformly, so that neither the temperature dependence of ρ nor the mobility R_H/ρ ($=e\tau/m$ for free electrons) is greatly changed with x. However, n_H increases more rapidly than the doping: A change from $x \equiv 0.11$ to 0.15 increases n_H (and decreases ρ) by a factor ~ 12 at $T=25$ K. Therefore, while transport measurements indicate that electron density increases with doping x, the increase is not linear. This

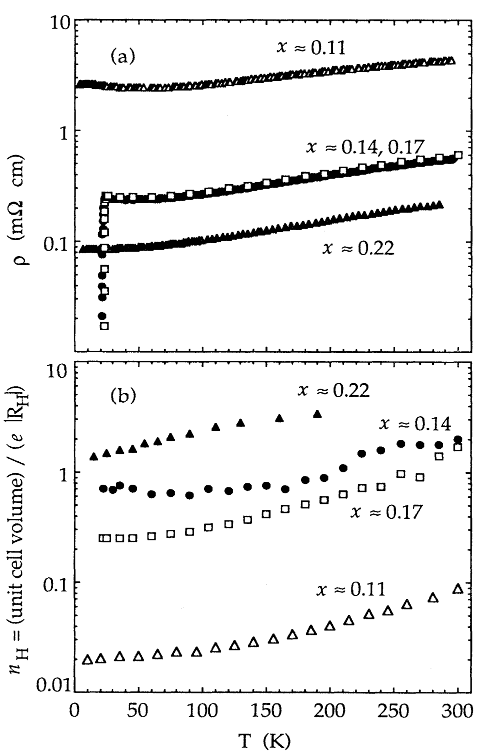

FIG. 3. (a) In-plane resistivity and (b) "Hall number" n_H vs temperature.

effect, seen also in x-ray absorption[6] and Hall[1] studies on ceramic $Nd_{2-x}Ce_xCuO_{4-y}$ and in doping studies on the p-type superconductors,[13] is at least partially due to changes in oxygen deficiency y with doping.

We find the same magnitude for ρ (300 K) in our $x=0.14$ and $x=0.17$ crystals as in the $x=0.16$ crystal of Ref. 8, but the resistivity ratio $\rho(300\text{ K})/\rho(25\text{ K})\sim 2$ in our superconducting crystals is smaller than the value (~ 6.9) reported in Ref. 8. Also, R_H ($T\approx T_c$) in our highest-T_c crystals is 60% as large as found in Ref. 8. The simplest interpretation of these differences is that our samples have a greater carrier density (but more residual scattering). Since the Ce dopings x of the superconducting crystals used in these two studies were nearly equal, different oxygen deficiencies y probably account for most of this difference in carrier density.

Thus our data confirm earlier transport results[1,8] on ceramics and $x=0.16$ crystals. We verify that in crystals with sharp and complete superconducting transitions the Hall coefficient is negative and excess doping changes the sign of R_H as it suppresses superconductivity (as in[9] the p-type $La_{2-x}Sr_xCuO_4$). Measurements on crystal samples therefore confirm that the transport properties of the n- and p-type cuprates respond symmetrically to doping. Because our microscopic characterization of these crystals, as well as magnetization and resistivity studies, indicate that these crystals are single phase and uniformly doped, we argue that this transport behavior reflects the intrinsic properties of the $R_{2-x}Ce_xCuO_{4-y}$ system.

While our results for superconducting crystals are similar to those of Refs. 1 and 8, they are quite different from those of Wang *et al.*,[7] who report R_H positive and strongly temperature dependent at low temperatures where ρ remains flat. Wang *et al.* propose that the temperature behavior they found for R_H and ρ suggests a two-band model in which electron and hole regions coexist on the Fermi surface, but where holes dominate R_H while electrons dominate ρ. They then argue that the hole carriers in $Nd_{2-x}Ce_xCuO_{4-y}$ resemble those in the p-type cuprate superconductors and are responsible for the superconductivity, and so the mechanism of superconductivity need not include the n-type carriers. While our Hall measurements confirm that two conduction bands may exist (R_H should be temperature independent in a one-band system), they contradict the assertion that holelike carriers with strongly temperature-dependent scattering dominate the Hall effect in the superconducting crystals. We find the temperature dependence of both R_H and ρ weakening at low temperature, and we find $R_H>0$ only in overdoped crystals. Therefore, we find no evidence that the hole carriers that dominate the Hall effect at large doping are necessary for superconductivity.

In summary, we have grown high-quality single crystals of the "n-type" superconductor $R_{2-x}Ce_xCuO_{4-y}$ ($R=$Nd and Sm) for a range of doping x and measured the Hall coefficients and resistivities for in-plane conduction. We find that R_H is negative in both lightly doped and superconducting samples: Increased Ce doping systematically reduces both the Hall coefficient and resistivity, consistent with a direct enhancement of the carrier density n. At high doping, R_H changes sign, as in the (holelike) $La_{2-x}Sr_xCuO_4$ system. Although the temperature and doping dependence of R_H suggests that both electron and hole carriers exist in this system, transport in the lightly doped and superconducting crystals is evidently dominated by the electrons.[16] The similarity between the response of the transport properties to Ce doping in this system and to Sr doping in $La_{2-x}Sr_xCuO_4$ constitutes strong evidence that the mechanism for high-temperature superconductivity in the copper oxides is symmetric under the replacement of electrons with holes.

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*Also at IBM Research Division, Yorktown Heights, NY 10598.

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[13]N. P. Ong, in *Physical Properties of High-Temperature Superconductors,* edited by D. M. Ginsburg (World Scientific, Singapore, 1990), Vol. II.

[14]See C. M. Hurd, *The Hall Effect in Metals and Alloys* (Plenum, New York, 1972).

[15]We also find a negative Seebeck coefficient (in plane) in these crystals at $T=300$ K, in agreement with Ref. 4, which is further evidence for predominantly electron conduction.

[16]During preparation of this manuscript, we learned of recent Hall-effect measurements by W. Sadowski *et al.* [J. Less-Commun. Met. **164-165**, 824 (1990)] in $Nd_{2-x}Ce_xCuO_{4-y}$ crystals with $x=0.15$. They confirm that $R_H<0$ in samples with sharp superconducting transitions.