Oxygen dependence of the transport properties of $Nd_{1.78}Ce_{0.22}CuO_{4\pm\delta}$

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(Received 16 June 1995)

We have investigated the transport properties of high-quality $Nd_{1.78}Ce_{0.22}CuO_{4\pm\delta}$ films as a function of oxygen concentration. Surprisingly we find superconductivity in films that are slowly cooled in vacuum from the deposition temperature. A systematic study of the effect of oxygen on resistivity, Hall effect, and thermopower suggests that extra oxygen introduces impurity scattering without changing the carrier density. Magnetoresistance data reveal that these impurities are spin disordered in nature. The spin impurities introduced upon oxygenation of the sample may be responsible for suppressing the superconductivity.

I. INTRODUCTION

The role of oxygen has been an important topic in cuprate superconductors. In many hole-doped cuprates, superconductivity can be induced by either cation or oxygen doping because oxygen strongly affects the carrier density and T_c.[1] However oxygen seems to play a different role in the *n*-type $Nd_{2-x}Ce_xCuO_{4\pm\delta}$ (NCCO) system where Ce doping alone cannot produce superconductivity.[2–4] The superconducting properties of NCCO are extremely sensitive to oxygen content: an as-grown NCCO crystal ($x=0.15$) is not superconducting and a small reduction of oxygen ($\delta\approx 0.01$–0.03) (Refs. 5 and 6) is necessary to induce superconductivity. Recent studies on NCCO thin films[7,8] have shown that the effect of changing oxygen content is not the same as Ce doping. It is therefore important to understand how oxygen variation affects superconductivity and how it differs from Ce doping.

Previous studies[2–4,9] on NCCO crystals and ceramics have shown that NCCO is only superconducting within a narrow Ce concentration ($x=0.14$–0.18). When it is ''overdoped'' with Ce to the solubility limit ($x=0.22$), the NCCO sample is metallic with no evidence of superconductivity.[10,11] However, the absence of superconductivity in Ce=0.22 samples is not well understood and the oxygen dependence of the properties of Ce=0.22 NCCO has not been studied in detail. From a naive picture, increasing oxygen content should have a similar effect as reducing Ce content, and possibly make the Ce=0.22 sample superconducting. Reducing the oxygen content should be similar to increasing Ce doping, which might allow us to study NCCO beyond the Ce solubility limit.

In this paper, we report systematic studies on resistivity, Hall effect, thermopower, and magnetoresistance (MR) in Ce =0.22 NCCO thin films with various oxygen content. We have found, for the first time, that Ce-overdoped NCCO films can be made superconducting when prepared by cooling from 800 °C to room temperature under vacuum. We also find that increasing the oxygen content in the films does not change the carrier density, in contrast with Ce doping.

II. EXPERIMENT DETAILS

NCCO thin films are grown from NCCO Ce=0.22 ceramic targets on various substrates ($LaAlO_3$, $SrTiO_3$, and YSZ, etc.) by pulse laser deposition in N_2O gas. The details of the deposition can be found elsewhere.[12] The typical film thickness is 1000 Å. The as-deposited film is cooled down naturally ($\sim$2 h) in vacuum from the deposition temperature ($\sim$800 °C) to room temperature to reduce the amount of extra oxygen. The NCCO ($x=0.22$) films grown by this method show superconductivity with a T_c ranging from 3 to 10 K. X-ray diffraction shows that the film is highly *c*-axis oriented. The *c*-axis lattice parameter indicates that the Ce concentration is $\sim 0.22\pm 0.01$ and is uniform over the film area (at least in regions larger than the x-ray beam size of ~ 1 μm).

For transport measurements, we patterned the film into a Hall-bar-shaped bridge with a film width of 100 μm. A low-frequency (17 Hz) ac method is used for resistivity, Hall effect, and MR measurements. ac susceptibility[13] is done by placing the primary coil and the pickup coil on the opposite sides of the film at a frequency of 60 kHz. The thermoelectric power is measured on a narrow film ($\sim$1 mm wide) using gold leads as the voltage probe with a slow ac method.[14] Gold wires from the same spool were calibrated against Pb foil (99.999% pure) by using the Pb data of Roberts.[15] Oxygenation of a film is achieved by annealing the film successively at 650, 680, 710, 740, 770, and 800 °C in an oxygen atmosphere for 1 h at a time. X-ray diffraction on oxygenated samples shows no measurable difference from that of the original sample. After each oxygenation step, transport properties are measured.

III. RESULTS AND DISCUSSION

Figure 1 shows the resistivity of a Ce overdoped NCCO film ($x=0.22$) before any oxygen treatment. Its ac susceptibility as a function of temperature is shown in the inset. Both resistivity and ac susceptibility show a superconducting transition at $\sim$10 K. The resistivity can be best fit to $\rho=\rho_0+AT^{\alpha}$, where $\alpha\approx 1.8$, a slightly smaller power than that of Ce=0.15 NCCO superconductors ($\alpha\approx 2.0$).[16,17] Electron-electron scattering results in a resistivity of $\rho\sim AT^2$ with a coefficient $A\sim 1/(\omega_P^2\tau_0 T_F)$,[18] where ω_p is the plasma frequency, τ_0^{-1} the bare scattering time, and T_F the Fermi temperature. When the Ce doping increases from

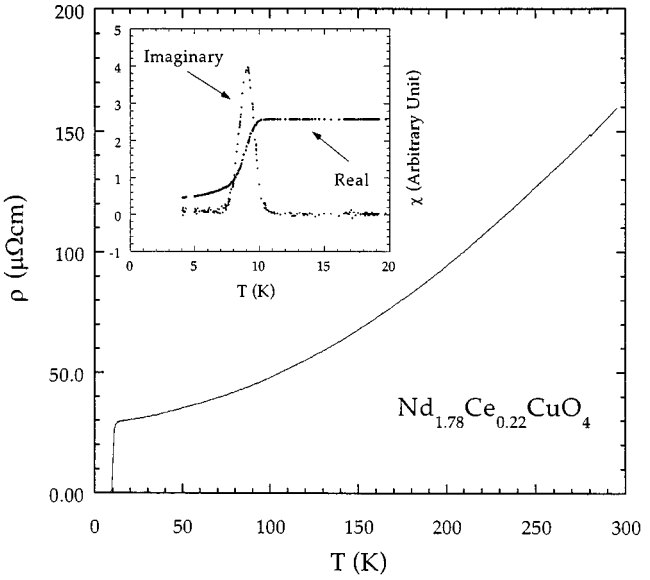

FIG. 1. In-plane resistivity vs temperature of a $Nd_{1.78}Ce_{0.22}CuO_4$ film, showing a superconducting transition near $T=10$ K. The inset shows the ac susceptibility vs temperature for the same sample.

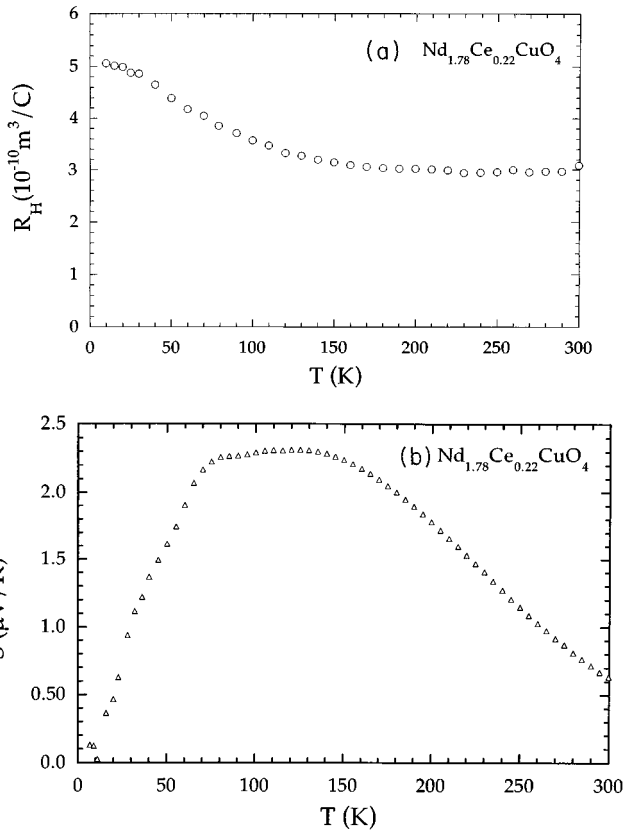

FIG. 2. (a) Hall coefficient vs temperature for the superconducting sample shown in Fig. 1. (b) Thermopower vs temperature for the same sample.

0.15 to 0.22 in NCCO the increased carrier density should lead to an increase in both T_F and ω_P (ignoring effective mass changes), which results in a smaller electron-electron scattering term. A fit of the resistivity data for the Ce=0.22 sample to $\rho=\rho_0+AT^2+BT$ yields a coefficient of $A=1.3\times10^{-3}$ $\mu\Omega$ cm/K^2, which is smaller than that of Ce =0.15 samples ($\sim3\times10^{-3}$ $\mu\Omega$ cm/K^2), in qualitative agreement with our expectation. The deviation of the resistivity from T^2 behavior in the Ce=0.22 samples indicates a contribution from a linear dependent term, e.g., electron phonon scattering. We measured the resistivity of a Ce=0.22 NCCO crystal from room temperature to 800 K.[19] The temperature dependence of the resistivity became close to linear at the highest temperature, indicating that electron-phonon scattering dominates the transport at high temperature.

Our observation of superconductivity in a vacuum cooled Ce=0.22 sample is rather surprising since previous measurements on as-grown NCCO crystals with Ce=0.22 did not reveal any superconductivity. We did not observe superconductivity in an oxygen reduced $x=0.22$ NCCO crystal either. One possibility is that oxygen in these bulk samples cannot be easily changed. In a film, however, besides the normal oxygen diffusion channels along the c axis and ab plane, grain boundary effects and strains caused by lattice mismatch between the film and the substrate may introduce additional diffusion channels,[20] making it easier to remove oxygen in a film than in a crystal or a ceramic sample. As shown in an earlier study[7] on the effect of oxygen in Ce=0.15 samples, some of the oxygen in a film can be removed at $\sim$600 °C in vacuum, compared with the much higher temperature ($\sim$950 °C) needed in crystals and ceramics. We have observed superconductivity on several Ce=0.22 samples that, from x-ray diffraction, are phase pure. If there exists trace amounts of a Ce=0.15–0.18 superconducting phase that is beyond the resolution of our x-ray diffractometer ($<5\%$) in these samples, we would not be able to detect a superconducting transition in the ac susceptibility measurement associated with these traces. Therefore we believe that the superconducting transition we observed is an intrinsic property of Ce=0.22 NCCO films. This result suggests that the range of Ce doping that results in superconductivity is wider than previously believed.

Figure 2(a) shows the Hall coefficient vs temperature for the same sample. The Hall effect is uniformly positive and does not exhibit the $1/T$ behavior found in p-type cuprates. The data are very similar to that of $x=0.22$ NCCO single crystals.[10] Figure 2(b) shows thermopower (S vs T) for the same sample. S is small and positive for the entire measured temperature range and nearly linear in T above 150 K, with a negative slope of $dS/dT\sim-0.011Z$ μV/K^2. The same positive signs of R_H and S indicate hole conduction in the Ce =0.22 NCCO film. The presence of a superconducting transition in the same sample indicates that holes may be responsible for the superconductivity in the NCCO films ($x=0.22$).

In Ce=0.15 NCCO, the Hall effect is negative and strongly temperature dependent while the Seebeck coefficient has a positive sign. There have been suggestions of a two-carrier conduction model.[7] In the Ce=0.22 NCCO, however, Hall effect is T independent for $T>150$ K and both the Hall effect and thermopower have the same sign. It is likely that there is only one conducting carrier.

Figure 3(a) shows the ρ vs T on a semilog scale for a Ce=0.22 NCCO sample when it is successively oxygenated. An arrow indicates the direction of oxygenation. We can see

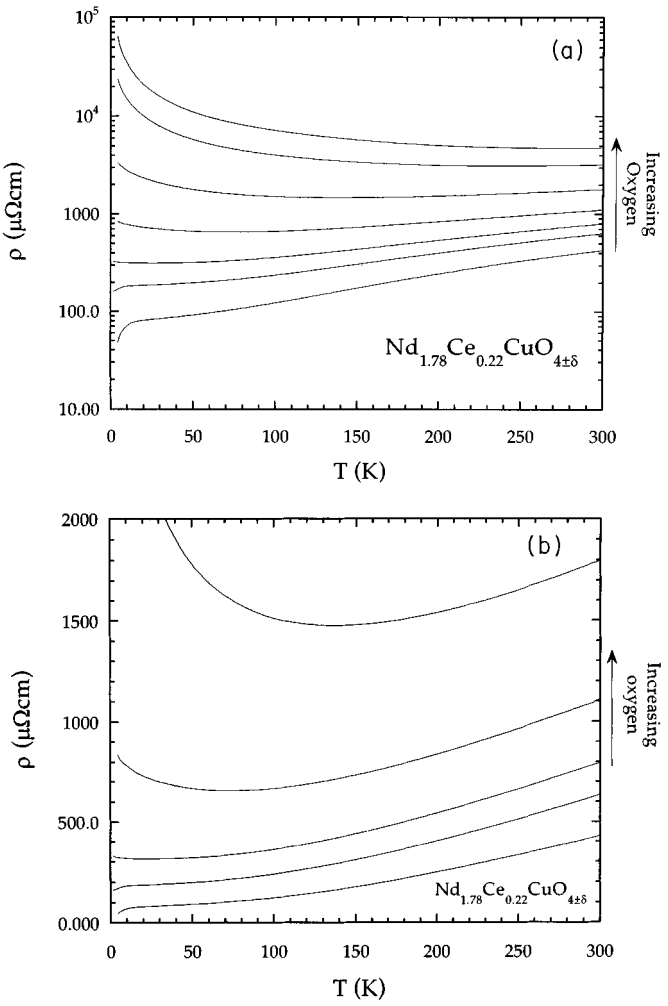

FIG. 3. (a) Resistivity vs temperature of a $Nd_{1.78}Ce_{0.22}CuO_{4\pm\delta}$ film with various oxygen content. The arrow indicates the direction of oxygenation. (b) The same plot for the first curves, except that the resistivity is on a linear scale.

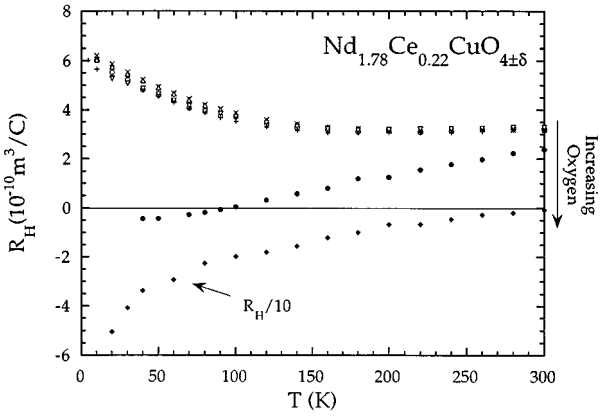

FIG. 4. Hall coefficient vs temperature of a $Nd_{1.78}Ce_{0.22}CuO_4$ film when it is successively oxygenated. The successive oxygenation temperatures are (∇) no oxygenation, (+) 650 °C, (△) 680 °C, (×) 710 °C, (○) 740 °C, (●) 770 °C, and (◆) 800 °C. The arrow indicates increasing annealing temperature.

that with increasing oxygen content the resistivity increases monotonically. Figure 3(b) shows the same plot on a linear scale for the first five curves. It can be seen that the change in the temperature-independent part of the resistivity is much greater than that of the temperature-dependent part for $T>150$ K. Therefore, the main effect of oxygenation on the resistivity is that it increases the impurity scattering of carriers while the change in carrier density or other scattering contributions remains relatively small. It can be seen from Fig. 3(b) that with oxygenation the metallic temperature dependence changes to a more semiconductorlike behavior at low temperature. When the sample is further oxygenated, as in the case of the last two curves in Fig. 3(a), ρ has negative slope at room temperature, indicating a strong localization of carriers.

Figure 4 shows the Hall effect vs temperature for these samples. Again an arrow indicates the direction of oxygenation. As we can see, the first five sets of data [corresponding to the data of Fig. 3(b)] virtually overlap one another for the entire measured temperature range. Their Hall effect is positive, and temperature independent above $T=150$ K, indicating holelike carriers in the system. The Hall number obtained from the measurements is ~2.8 holes/formula unit, an order of magnitude larger than the Ce doping ($x=0.22$). This discrepancy is not surprising since $R_H=1/ne$ only holds for a single parabolic band. Our previous study on NCCO films[7] with $x=0.15$ showed that the Hall effect for the best superconducting film is strongly temperature dependent and that it crosses over to a positive value upon deoxygenation. This suggested that both holes and electrons might be present in the highest T_c sample. In our Ce=0.22 NCCO films, the Hall coefficient for the superconducting samples is uniformly positive for the measured temperature range.

It is surprising to see that the Hall coefficient remains the same when oxygen is added to the sample while the corresponding resistivity for the first five curves [see Fig. 3(b)] changes by as much as a factor of 4 at room temperature. Earlier Hall effect measurements[10] have shown that the Hall coefficient is very sensitive to the level of Ce doping. It changes from a positive value in a Ce>0.15 sample to a negative value for a Ce<0.15 sample, while the magnitude of R_H increases as the Ce doping decreases, consistent with a decreasing carrier density n. In a simple picture, reducing the Ce doping will have the same effect as increasing oxygen content in NCCO. However, the addition of extra oxygen in our Ce=0.22 films does not seem to change the carrier density immediately. With further oxygenation, the Hall effect changes to a negative value and the magnitude of the Hall coefficient increases, exhibiting a similar trend as reducing Ce. This is the region where the carriers appear to be localized.

While the linear temperature dependence of resistivity and $1/T$ dependence of Hall coefficient in many hole-doped cuprate superconductors are difficult to explain in a Fermi-liquid theory, the resistivity and Hall effect of Ce=0.15 or Ce=0.22 NCCO are both consistent with Fermi-liquid theory. The resistivity of both Ce=0.15 and Ce=0.22 NCCO can be interpreted as a combination of electron-electron scattering and electron-phonon scattering. The Hall effect of Ce =0.22 NCCO is temperature independent above 150 K. And even though the Hall effect of Ce=0.15 NCCO is strongly T dependent, it has been explained by conventional two-carrier conduction.[7]

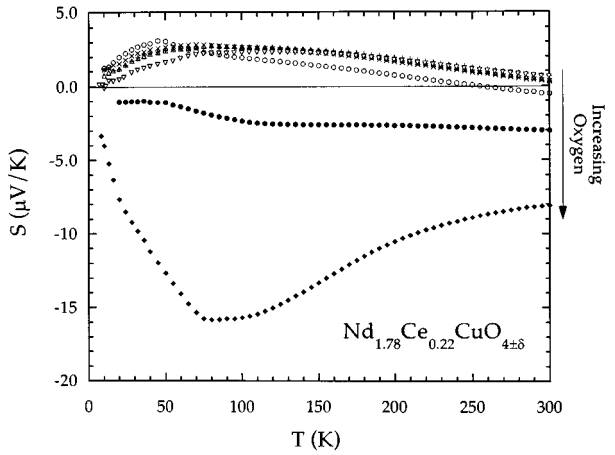

FIG. 5. Thermopower vs temperature of a $Nd_{1.78}Ce_{0.22}CuO_4$ sample under the same oxygen treatment as the Hall effect measurement. The successive oxygenation temperatures are (∇) no oxygenation, (+) 650 °C, (△) 680 °C, (×) 710 °C, (○) 740 °C, (●) 770 °C, and (♦) 800 °C.

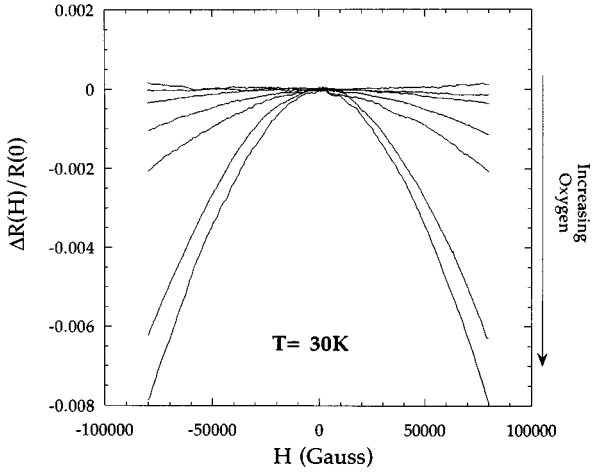

FIG. 6. Magnetoresistance vs magnetic field ($H \| J_{ab} \| ab$ plane) at $T = 30$ K of a $Nd_{1.78}Ce_{0.22}CuO_4$ film when it is successively oxygenated.

To further probe the effect of oxygen variation we carried out thermopower measurements on a similar film. The same oxygen treatment is applied to this sample and the thermopower is measured after each oxygenation step. Figure 5 shows S vs T for the sample with an arrow indicating the direction of oxygenation. The first four curves are overlapped for $T > 80$ K. They are uniformly positive and has the same sign as that of the Hall effect. The fifth curve shifts down slightly from the first four sets of data,indicating the onset of a change in carrier density. The small differences among the first five curves for $T < 80$ K may be caused by a slightly different impurity level in the sample, as impurity content usually affects the thermopower of metals at low temperature. In agreement with the Hall effect data, the thermopower data show that the excess oxygen is not changing the carrier density and that the carriers are holelike. Thermopower has been shown to be sensitive to the Ce concentration in NCCO. According to an earlier experiment,[21] as the Ce doping decreases, the thermopower changes from a positive value to a negative value. So the general trend for reducing Ce and increasing oxygen in NCCO is the same.

It is interesting to note that both the magnitude and temperature dependence of the thermopower of our samples resemble those of many hole-type superconductors.[22] This may be another indication that carriers in Ce overdoped NCCO may be the same as those in hole-doped superconductors. When more oxygen is added to the sample S changes to a negative value, the same trend as that of the Hall coefficient.

We have seen from our measurements of ρ, R_H, and S on Ce=0.22 NCCO films that oxygenation initially increases the impurity level without changing the carrier density. In hole-doped cuprates, oxygen content affects the carrier density as well as the superconducting transition temperature of a sample. For example, when oxygen is depleted from a $YBa_2Cu_3O_7$ sample, the carrier density as well as the transition temperature decreases. In our Ce=0.22 NCCO films, however, a small amount of excess oxygen can suppress superconductivity even though the carrier density is not affected.

A universal feature of all the high-T_c cuprates is that they start from an antiferromagnetic (AFM) insulator. AFM is suppressed by carrier doping and superconductivity occurs in a certain range of doping. In the hole-doped cuprates, a doped hole goes to the oxygen site.[23,24] The spin resulting from a hole at the oxygen site may cause ''spin frustration'' for the neighboring Cu^{2+} ions.[25] This is why hole doping suppresses the Cu-Cu AFM spin correlation rapidly. Since a doped electron prefers to go to the Cu site, creating the nonmagnetic ion Cu^{+}, the AFM spin of Cu^{2+} is only diluted when Ce is doped in NCCO (Ref. 26) and local spin correlations should be present even at the highest Ce doping level. This has recently been confirmed by a Raman scattering experiment[27] which has shown that the local AFM order does not decrease with increasing Ce doping. Thus, there are indications for local spin correlations in NCCO, even for the overdoped Ce samples.

The interaction between conducting electrons and spin impurities can result in a negative MR.[28] However, when the

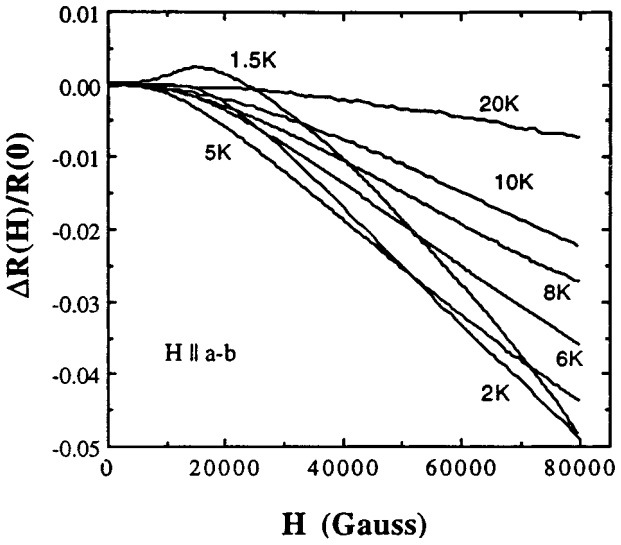

FIG. 7. Magnetoresistance vs magnetic field ($H \| J_{ab} \| ab$ plane) for a fully oxygenated $Nd_{1.85}Ce_{0.15}CuO_4$ film at various temperatures.

current is in the ab plane and the magnetic field is parallel to it, there will be no contribution to MR either from the classic MR or from two-dimensional (2D) weak localization. Figure 6 shows our MR data at $T=30$ K for $H\|J_{ab}$ on the same Ce=0.22 sample in which we measured the Hall effect. At this temperature, the effect of superconducting fluctuations can be ignored. A negative MR starts to appear when the sample is oxygenated. These data indicate that any spin-scattering effect is very small before the oxygenation. But upon oxygenation, the spin-scattering effect gets more and more important. Figure 7 shows the MR vs field in the same geometry for a fully oxygenated nonsuperconducting Ce =0.15 film. A negative MR is also present for $T\leqslant 20$ K. It is likely that the impurities generated by the extra oxygen are spin (magnetic) impurities in both the Ce=0.15 and C=0.22 samples. Therefore superconductivity may be suppressed by the spin impurities introduced by extra oxygen. This would be consistent with the s-wave nature of the superconductivity in NCCO as found from penetration depth measurement.[29] Our experiments to determine the number of spin impurities by an electron spin resonance (ESR) experiment on our films failed.

Interstitial oxygen in as-grown $Nd_2CuO_{4+\delta}$ crystals has been seen by a neutron-scattering experiment.[30] These interstitial oxygen reside in the apical site and can be removed through deoxygenation of the crystals. Although a similar neutron-scattering experiment on the Ce=0.15 or Ce=0.22 samples has not yet been done it is possible that interstitial oxygen also exists in the oxygenated Ce=0.15 and Ce=0.22 NCCO samples, causing spin impurities, which in turn suppresses the superconductivity.

IV. SUMMARY

In summary, we have observed superconductivity in $Nd_{1.78}Ce_{0.22}CuO_{4+\delta}$ films cooled slowly in vacuum from deposition temperature (800 °C) to room temperature. We also have systematically studied the resistivity, Hall effect, and thermopower of Ce=0.22 NCCO films when they are oxygenated. We find that oxygenation increases the impurity scattering in the films, but the carrier density is not affected. The impurities introduced by the extra oxygen cause spin scattering of carriers, as shown in a magnetoresistance measurement. These magnetic impurities may suppress superconductivity and an oxygen reduction process appears to remove these spin impurities to allow superconductivity.

ACKNOWLEDGMENTS

We would like to thank Tom Clinton and X. J. Jiang for several useful discussions. This work was supported by NSF under Contract No. DMR 9209668.

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