Destruction of superconductivity in $Nd_{2-x}Ce_xCuO_{4-\delta}$ thin films by ion irradiation

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We have measured the resistivity and Hall coefficient of $Nd_{2-x}Ce_xCuO_{4-\delta}$ (NCCO) thin films sequentially damaged by ion irradiation. The T_c of the NCCO decreases linearly with residual resistivity and extrapolates to zero at $R_{\square}/(\text{unit cell})\approx 5-10$ kΩ, results similar to Y-Ba-Cu-O. We suggest that the physical basis for this behavior in NCCO may be disorder effects in a homogeneous two-dimensional superconductor. Unusual behavior of the Hall coefficient gives further evidence that NCCO may be a two-carrier conductor. [S0163-1829(98)04537-8]

I. INTRODUCTION

The electron-doped cuprate superconductor $Nd_{2-x}Ce_xCuO_{4-\delta}$ (NCCO) exhibits differences from the more extensively studied high-T_c hole-doped cuprates in both its normal state and superconducting properties. Several studies[1–3] imply that NCCO may be a more conventional, BCS-gapped superconductor within a class of materials with an exotic pairing function. This makes NCCO a key perovskite oxide superconductor to understand: elucidating its properties could determine whether the mechanism for pairing in the planes is crucial for the high T_c's of the cuprates.[4]

We have probed the superconducting and normal states of NCCO in a series of transport experiments on ion-irradiated thin films. By measuring resistivity $\rho(T)$ and Hall coefficient $R_H(T)$ of NCCO films as point defects are introduced, it is possible to study how superconductivity is destroyed. Results can be compared with previous ion damage studies on Y-Ba-Cu-O.[5,6] These studies showed that the superconductivity of Y-Ba-Cu-O is much more robust with respect to disorder than expected for a pure d-wave superconductor. Preliminary studies on NCCO suggested that its dependence of T_c on damage is similar to that of Y-Ba-Cu-O and other hole-doped cuprates.[7,8]

Here we present data on a set of films that exhibit a continuous destruction of superconducting behavior with increasing ion damage. A small amount of ion-induced disorder raises the residual resistivity and decreases the T_c. At higher fluences, resistivity rises rapidly at low temperatures due to a combination of increased scattering and carrier freezeout. Disorder induced a drop in T_c which showed strong similarities to results in Y-Ba-Cu-O despite significant qualitative difference in the resistivity and Hall coefficient (as a function of temperature) of NCCO and Y-Ba-Cu-O.

II. EXPERIMENTS AND RESULTS

We prepared c-axis-oriented NCCO thin-film samples by pulsed-laser ablation. One set of films was grown 1000 Å thick using a target with initial [Ce]=0.15 and was damaged with 200 keV Ne^+ ions. A second set was grown 4000 Å thick using a target with initial [Ce]=0.14 and was damaged with 200 keV He^+ ions.

All films were grown using a KrF (248 nm) pulsed excimer laser focused to an intensity of approximately 1.6 J/cm^2. Deposition took place in a 180 mT N_2O atmosphere on yttria-stabilized zirconia (YSZ) substrates held at 820 °C. A vacuum post-anneal during cooldown adjusted oxygen doping to optimize film properties. All samples were patterned into Hall bars 100 μm wide with 300 μm between voltage arms using photolithography and ion milling. Low resistance contacts were made by evaporating silver contact pads after etching the NCCO surface with a 4% HCl solution.

Films were irradiated by either 200 keV Ne^+ (1000 Å thick films) or He^+ ions (4000 Å thick films). The thicknesses of the films were chosen so that the ions would have enough energy (as calculated by TRIM simulation[9]) to pass entirely through the NCCO and embed in the YSZ substrate. Passing the ions through the material promotes uniformity of damage throughout the film thickness.

At each level of damage $\rho(T)$ was taken by a standard four-point ac lock-in technique at low frequency and 1 μA excitation current. Hall measurements of $R_H(T)$ were made at a field of 8 T by the same four-point ac lock-in technique. The upper critical field of NCCO at zero temperature is 8 T, so anomalous Hall effects from vortex motion should not be observed in our data. This relatively low $H_{c2}(0)$ makes it possible to measure normal-state carrier behavior in NCCO below T_c, an advantage over many of the hole-doped cuprates which display extraordinarily large values for H_{c2}.

Figure 1(a) shows a series of resistivity curves for a sequence of damage levels measured for three films with [Ce]=0.14. At temperatures above 150 K, all curves (until the most damaged) are approximately parallel and thus only differ by a temperature-independent residual resistivity. This implies that the ion damage simply introduces defect scattering centers and that the oxygen doping of the NCCO is not affected by the damage (changing oxygen doping changes the temperature dependence of resistivity in the normal state). The resistivity curves above 150 K obey Matthiessen's rule with $\rho(T)=\rho_o+A(T)$, where $A(T)$ is approximately constant over damage levels and ρ_o increases monotonically with ion fluence. All our data can be well fit by either $A(T)=aT+bT^2$ with $bT^2>aT$ or $A(T)=\alpha T^{\beta}$ with $\beta\approx 1.7$. From these fits we can extract ρ_o for each level of damage. Figure 1(b) illustrates some of these fits. Figure 1(c) shows resistivity on a log scale for higher levels of damage.

At lower temperatures (i.e., below 150 K), increased ion fluence changes the temperature dependence of the resistivity as the NCCO is driven nonsuperconducting by disorder. Fig-

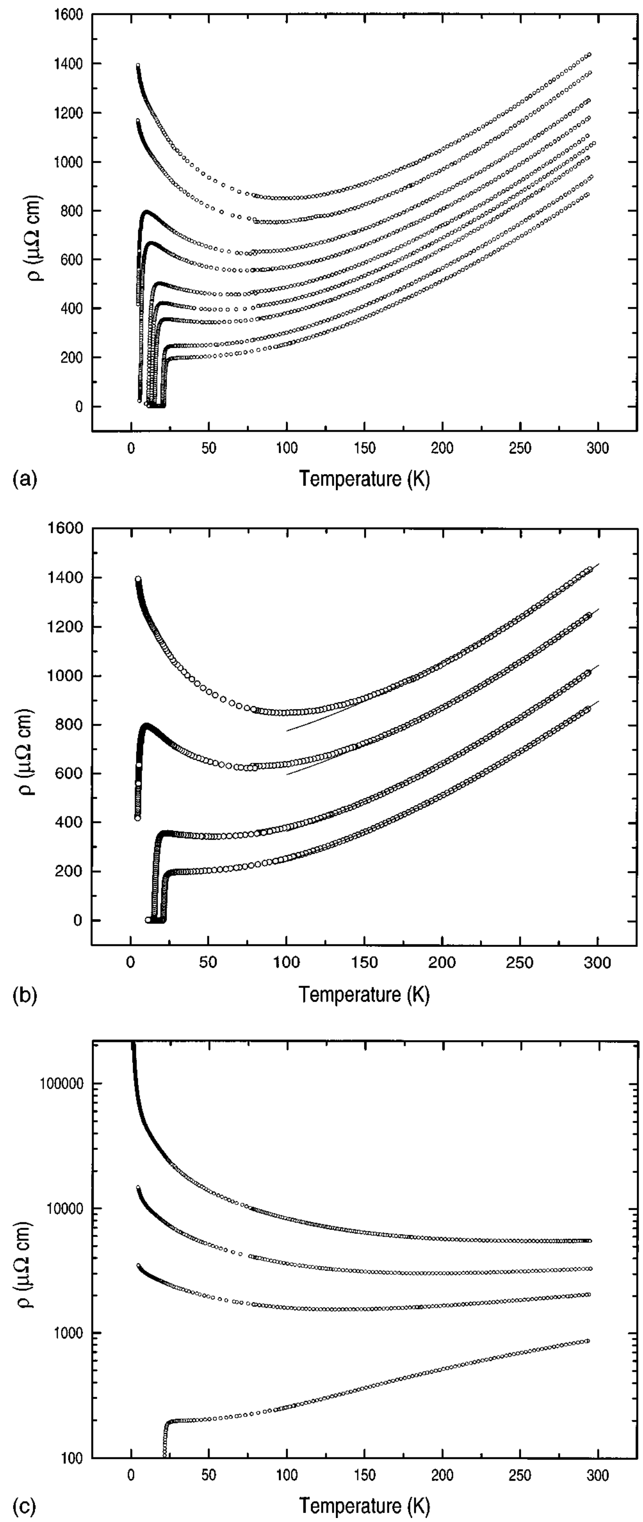

FIG. 1. (a) Resistivity as a function of temperature for NCCO ([Ce]=0.14) films damaged with He^{+} ions. From bottom to top, ion fluences are 0, 0.5, 1, 1.5, 2, 2.5, 3, 4, and 4.5×10^{14} ions/cm^2. (b) Representative fits of resistivity data to the function $\rho(T)=\rho_o+\alpha T^{\beta}$, with $\beta\approx1.7$, over the range $T=100-300$ K. (c) Resistivity as a function of temperature for NCCO ([Ce]=0.14) films at high levels of ion damage. From bottom to top, ion fluences are 0, 6.5, 12.5, and 18.5×10^{14} ions/cm^2.

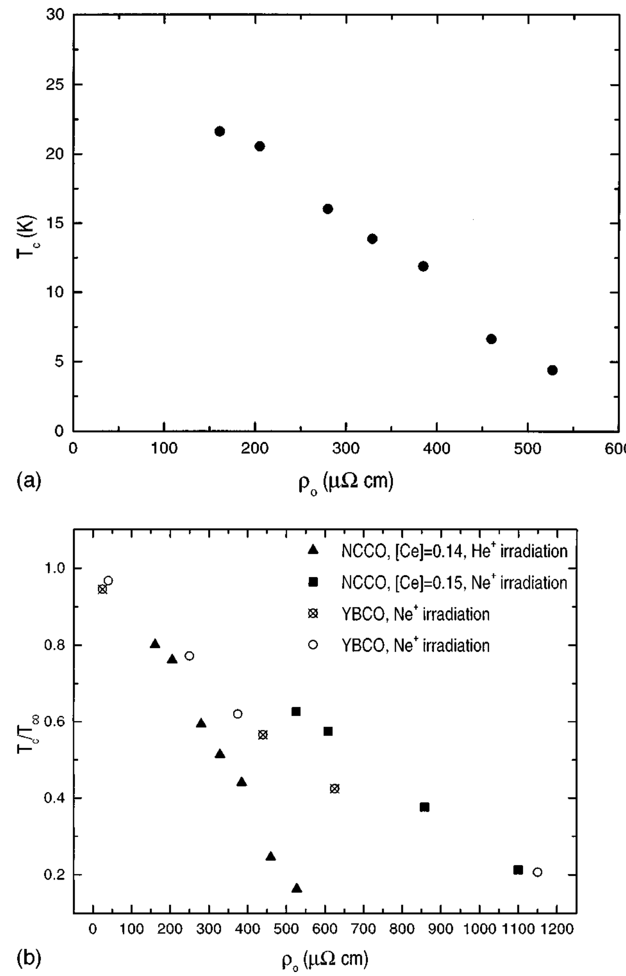

FIG. 2. (a) T_c of NCCO ([Ce]=0.14) films as a function of residual resistivity. Note the linear dependence with T_c extrapolating to zero near 600 $\mu\Omega$ cm. (b) Scaled T_c's of ion-damaged NCCO and Y-Ba-Cu-O films as a function of residual resistivity. The two Y-Ba-Cu-O films were grown and damaged using the same facilities as our NCCO films.

ure 2(a) shows how T_c (measured at the midpoint of the resistive transition) is depressed toward zero with increasing residual resistivity caused by damage. The superconductive transition widths increase somewhat with damage but remain relatively sharp. As shown in Fig. 2(b), the dependence of T_c on ρ_o is similar to that seen in Y-Ba-Cu-O (scaling T_c by T_{co} in the undamaged material) and thus suggests a similar mechanism for destruction of superconductivity in these two materials. In particular, the critical ρ_o where the materials become nonsuperconducting is similar and both curves show an approximately linear dependence of T_c on ρ_o.

Companion Hall data for numerous damage levels on a single sample are shown in Fig. 3. R_H(T) for all temperatures and damage levels is negative in sign, implying nominal electron carriers for the NCCO films. The $R_H(T)$ curves show complicated behavior as a function of both damage and temperature. The high-temperature value of $|R_H(T)|$ decreases with damage monotonically but at low temperatures $|R_H(T)|$ decreases to a minimum and then increases. For all samples the amplitude of the Hall resistivity shows a trend from concave down to concave up at low temperatures with increasing damage. As will be discussed, the behavior of the

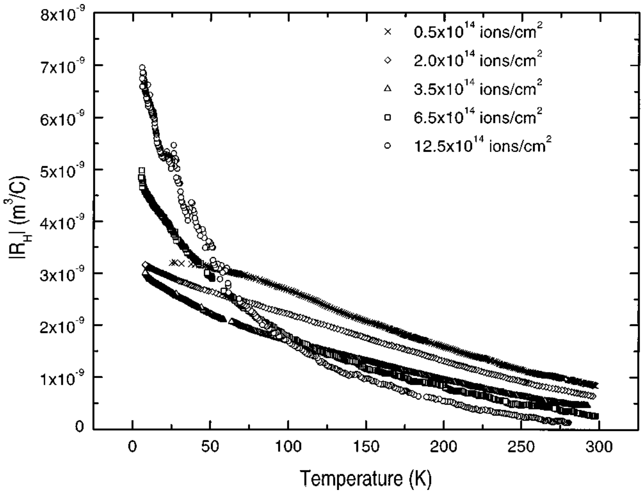

FIG. 3. Hall coefficient as a function of temperature for a single NCCO ([Ce]=0.14) film sequentially damaged with He^+ ions. All NCCO films exhibited negative R_H for all temperatures and for all levels of damage. At room temperature, $|R_H|$ decreases monotonically with damage.

Hall coefficient in these NCCO films can possibly be explained by invoking a two-carrier model.

III. DISCUSSION

Two prominent results of this experiment are the dependence of T_c on ρ_o as induced by ion damage and the unusual dependence of the Hall coefficient in NCCO on temperature and damage. The T_c vs ρ_o behavior in NCCO is similar to that in Y-Ba-Cu-O despite many differences in their electronic properties. Explanations of T_c vs ρ_o in Y-Ba-Cu-O in the literature depend on pair-breaking from scattering or on superconducting phase fluctuations, explanations that do not extend in a straightforward way to NCCO. The data suggest a different physical basis for the ρ_o dependence of T_c in both Y-Ba-Cu-O and NCCO: destruction of superconducting pair amplitude by disorder in a two-dimensional superconductor. This model requires only planar superconductivity, a property Y-Ba-Cu-O and NCCO have in common.

The dependence of T_c on ρ_o gives a simple measure of how superconductivity depends on disorder. In an ideal three-dimensional isotropic s-wave superconductor T_c should be unaffected by elastic nonmagnetic scattering according to Anderson's theorem. An ideal d-wave superconductor, on the other hand, should have a T_c strongly dependent upon nonmagnetic scattering because this scattering disrupts the k-space distribution of the pair potential associated with superconductivity, introducing pair breaking. Magnetic scattering strongly affects T_c in both the s-wave and d-wave cases. In ion damage experiments, Y-Ba-Cu-O and NCCO fall between these extremes: they are sensitive to nominally nonmagnetic scatterers (and T_c is driven to zero as scatterers increase) but they are much less sensitive to disorder than predicted for d-wave superconductors[6] (or for both s-wave and d-wave superconductors if the defects are magnetic). In any two-dimensional (2D) superconductor, increased scattering lowers T_c and destroys superconductivity at a characteristic sheet resistance. Single particle states are spatially localized in a 2D material and when the localization length becomes shorter than the superconducting coherence length, superconductivity collapses, and is replaced by insulating behavior.

For both NCCO and Y-Ba-Cu-O, T_c shows a near-linear dependence on ρ_o, and T_c extrapolates to zero at residual resistivities between 500 and 2500 $\mu\Omega$ cm. These two materials, however, show many differences in their superconducting properties and normal-state transport. Evidence from surface impedance measurements imply NCCO has a well-defined gap[1] consistent with an isotropic s-wave superconductor.[10] Tunneling studies also imply that the gap in NCCO is well-defined and excitations consistent with phonons take part in superconductivity.[11,12] Numerous experiments, on the other hand, have shown Y-Ba-Cu-O to be a mixed symmetry superconductor with a dominant d-wave order parameter.[13–15] In the normal state, NCCO shows a superlinear temperature dependence for resistivity, whereas Y-Ba-Cu-O exhibits linear background resistance. NCCO is doped with electrons and exhibits negative R_H (for [Ce] near the optimum value 0.15), and Y-Ba-Cu-O is doped with holes and exhibits positive R_H. The symmetry of the order parameter and the specifics of carrier scattering, therefore, do not seem to crucially impact the dependence of T_c on ρ_o in these cuprates.

Two possible explanations for the T_c vs ρ_o curve can be discounted in NCCO, although they have been advanced to describe similar results in Y-Ba-Cu-O. The first mechanism is destruction of superconductivity in a d-wave superconductor by nonmagnetic scattering.[16,17] If NCCO is an isotropic s-wave superconductor, this mechanism does not apply. But even if NCCO is forced to fit to such a model, the fitted value for the plasma frequency ω_p is 0.32 eV, a value one-third that found in optical measurements.[18] The second discountable mechanism is destruction of superconductivity in a ''bad metal'' by phase fluctuations.[19,16] As pointed out by Emery and Kivelson, the bulk T_c of NCCO should not be affected by phase fluctuations and is determined chiefly by its mean-field transition temperature.[20] Any explanation for T_c vs ρ_o for NCCO must lie elsewhere, and thus, given its similarity to T_c vs ρ_o in Y-Ba-Cu-O, so may the explanation for Y-Ba-Cu-O.

Both NCCO and Y-Ba-Cu-O are composed of stacks of coupled conductive copper-oxygen planes with a unit cell approximately 12 Å high. This two-dimensional nature suggests that the T_c dependence on disorder in these materials can be compared to the superconductor-insulator transition in disordered 2D films.[23,24] In fact, two-dimensional superconducting films exhibit a transition from superconductor to insulator at a resistance-per-square approximately equal to $h/4e^2 \approx 6500\ \Omega$. For our two sets of NCCO films, the critical $R_\square$-per unit cell where T_c extrapolates to zero are approximately 5000 and 12 000 Ω. Values between 8000 and 25 000 Ω are seen for Y-Ba-Cu-O.[25,16,5] It therefore seems plausible that superconductivity is destroyed by dimensional constraints in a disordered material, modulated somewhat by interlayer coupling. Given that superconducting transition widths remain relatively sharp with increasing damage in our NCCO resistivity curves, the model system for comparison should be a homogeneous (not granular) two-dimensional film.

Before concluding discussion on the T_c vs ρ_o data it is important to note that there is not yet definitive proof that the nature of superconductivity in NCCO and Y-Ba-Cu-O is dissimilar. Although there are obvious differences between the two materials, there is not yet consensus on the symmetry of the order parameter in NCCO. It has been argued that the activated surface impedance data in NCCO can result from disorder effects in a d-wave superconductor.[21] None of the tunneling data on NCCO shows perfectly classic BCS s-wave structure. Infrared transmission data shows non-BCS behavior of the superconducting gap in NCCO.[22] Our results could support the argument that NCCO is more similar to than different from the other superconducting cuprates.

The Hall coefficient for our films has significant dependence on temperature and - $1/R_H ec = 10^{21} - 10^{22}$ cm^{-3} as in Y-Ba-Cu-O. Otherwise it displays unusual behavior all its own. $|R_H|$ increases as temperature decreases for all damage levels, and $|R_H|$ changes from concave down to increasingly concave up at low temperatures as disorder increases. At high temperatures, $|R_H|$ surprisingly decreases with damage. At low temperatures, $|R_H|$ initially decreases with damage and then increases as its concavity changes. In Y-Ba-Cu-O R_H increases monotonically with disorder as would be expected if R_H were inversely proportional to free carriers.[5]

A possible explanation for the behavior of R_H in these NCCO films is that two bands contribute carriers; i.e., there is significant conduction by both holes and electrons, with electrons dominating [$R_H(T)$ is negative]. If more hole carriers than electron carriers are destroyed by damage, R_H will become more positive; i.e., $|R_H|$ will decrease. Actually, in a two-carrier model $|R_H|$ can decrease even if relative numbers of carriers stay the same and only scattering changes.[26] Previous studies in NCCO have invoked a two-carrier model to explain unusual characteristics of R_H.[27,28] Holes seem to contribute noticeably to R_H at high temperatures where R_H is balanced in negative and positive contributions and is thus very small and can decrease with damage. Electrons seem to dominate at low temperatures where R_H is very negative and $|R_H|$ increases monotonically for most levels of damage.

IV. SUMMARY AND CONCLUSIONS

We have studied, through resistivity and Hall measurements, how superconductivity is destroyed by disorder in NCCO thin films sequentially damaged by ion irradiation. At low fluences, this irradiation increases scattering by introducing defects without significantly changing the carrier density. Figure 4 shows that $1/\mu_H = \rho/R_H$ (proportional to scattering rate) increases monotonically while -$1/R_H ec$ is relatively constant as a function of increasing ion fluence. Despite their electronic differences, NCCO and Y-Ba-Cu-O show a similar dependence of T_c on ρ_o, indicating that the same mechanism destroys superconductivity in these two materials. The data implies that disorder effects in homogeneous two-dimensional superconducting systems may hold the key to understanding the destruction of superconductivity in NCCO and Y-Ba-Cu-O at approximately $R_\square$/(unit cell) $= h/4e^2$. The data give further evidence for two-carrier conduction in NCCO and suggest that electron transport dominates at low temperature, especially in disordered samples.

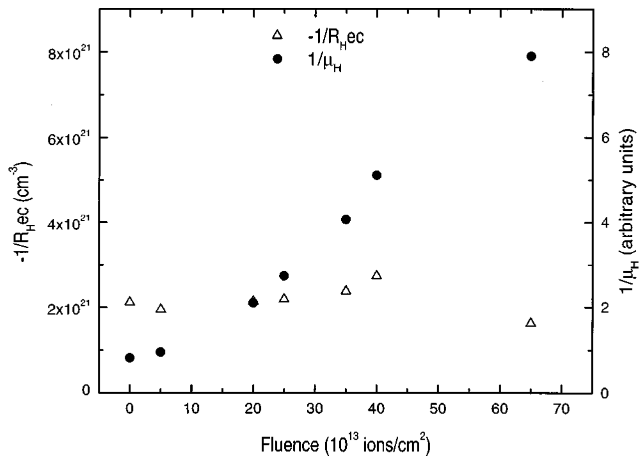

FIG. 4. Comparison of -$1/R_H ec$ and $1/\mu_H$ as a function of ion fluence at $T = 25$ K for NCCO ([Ce]=0.14) films. The inverse Hall resistance remains relatively constant while the inverse Hall mobility increases by over an order of magnitude. At this temperature, electrons seem to dominate the Hall measurement.

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