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Systematic variation of transport and thermodynamic properties with degree of reduction in $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$

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(Received 9 July 1990; revised manuscript received 23 April 1991)

Superconductivity only occurs in $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$ after heat treatment in a reducing atmosphere; yet we find the oxygen loss during reduction to be remarkably small. To better understand the physical role of reduction, we have systematically varied the degree of reduction in a series of ceramic samples by varying the partial pressures of oxygen and argon in the reducing atmosphere, keeping the total pressure constant. We find that small increases in the degree of reduction strongly increase the apparent carrier density and the superconducting Meissner fraction. We also find that there is an optimal degree of reduction to produce a single-phase sample with a zero-resistance superconducting state. These results call into question many previous experiments performed on samples of $Nd_{2-x}Ce_xCuO_{4-\delta}$ in which the effect of varying the degree of reduction was not systematically studied.

As-grown samples of the *n*-type copper oxide superconductor $Nd_{2-x}Ce_xCuO_{4-\delta}$ are not superconducting; superconductivity appears only after heat treatment in a reducing atmosphere.[1-4] Surprisingly, however, the change in oxygen off-stoichiometry δ with reduction is puzzling small, leaving the physical change brought about by reduction unexplained. Further, although some degree of reduction is required to induce superconductivity, excessive reduction has also been observed. Specifically, *n*-type single crystals of $Nd_{2-x}Ce_xCuO_{4-\delta}$ heat treated in a pure reducing atmosphere do not exhibit zero resistivity, despite large Meissner fractions.[3,4]

To better understand the physical role of reduction we have varied the degree of reduction in ceramic samples of $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$ by varying the partial pressures of oxygen and argon in a reducing atmosphere while keeping the total pressure constant. Ceramic samples have been studied instead of single crystals for their relative ease in uniformly reducing the samples, the tendency of single crystals to exhibit Ce and O concentration gradients[5] and to allow comparison with previous work on ceramics[1] for several different x (but only one reducing method). We show that increasing the degree of reduction strongly increases the apparent carrier density and the superconducting Meissner fraction. We also find that there is an optimal degree of reduction to produce a sample with a zero resistance superconducting state.

Unreduced samples of $Nd_{2-x}Ce_xCuO_{4-\delta}$ were prepared by solid-state reaction from high purity (99.99%) Nd_2O_3, CeO_2, and CuO. A stoichiometric mixture of starting materials was ground thoroughly and heated in an Al_2O_3 crucible at 950 °C for 20 hr in air. The resulting powders were reground and pressed into pellets. The pellets were sintered in air at 1100 °C for 10 hr and then cooled to room temperature over a period of 10 hr.

In Fig. 1 we show x-ray diffraction measurements (using Cu $K\alpha$ radiation) for a sintered pellet after surface scraping, the same sintered pellet, as grown, and the presintered calcined powder, before regrinding and pressing into the pellet. The trace amounts of $Nd_2Ce_2O_7$ and unreacted CuO present in the presintered calcined powder are absent in the (slowly cooled) scraped sintered pellet, which has the expected tetragonal T' structure with lattice parameters $a=3.947$ Å and $c=12.073$ Å.

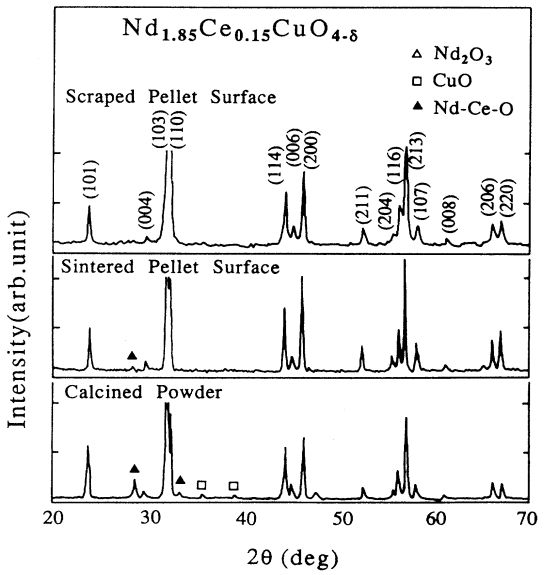

FIG. 1. X-ray diffraction measurements for a sintered pellet after surface scraping, the same sintered pellet, as grown, and the presintered calcined powder, before regrinding and pressing into the pellet. The pellet was sintered for 10 hr in air at 1000 °C followed by slow cooling over 10 hr to room temperature. The second phases and unreacted compounds present in the presintered calcined powder are absent in the scraped sintered pellet. Miller indices for $Nd_{1.85}Ce_{0.15}CuO_4$ are indicated in parentheses.

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The lattice parameters for $x=0.15$ (and their variation with x) have been measured against an internal silicon standard with $a=5.430\,88$ Å.

After sintering, the pellets were reduced by one of two different methods. In the first method, pellets were reduced for 24 hr at 900–950 °C for 24 hr in a pure argon (99.99% or 99.9995%) atmosphere. While pellets reduced for 20–24 hr exhibited significantly larger superconducting Meissner fractions than those annealed for 5–10 hr, no further increase in the superconducting Meissner fraction was observed for longer annealing times up to 200 hr. X-ray diffraction on sintered pellets with $x=0.15$ reduced in pure argon at $T\geq 1000$ °C show evidence of surface impurities and partial sample decomposition, while pellets reduced at $T\leq 950$ °C show no such evidence. In the second method, pellets were reduced for 20 hr at 1050 °C in an Ar-O_2 gas mixture with oxygen partial pressures varying from 5×10^{-4} to 10^{-4} to 10^{-1} atm, followed by quenching to room temperature in the same reducing atmosphere. X-ray diffraction on annealed scraped pellets again show no evidence for impurities, second phases, or sample decomposition.

We have monitored the variation in oxygen off-stoichiometry δ as $P(O_2)$ was changed by an inert gas fusion nondispersive IR method, but no systematic change was observed within our relative error in δ of 0.05. By successive thermogravimetric-analysis (TGA) measurements (5 °C/min up to 1000 °C) on a 167.5-mg sintered unreduced sample in pure argon (99.9995%), pure oxygen (99.99%), and pure argon, we find a reversible change in mass of 0.15 ± 0.05 mg at 950 °C, equivalent to a change in oxygen off-stoichiometry $\delta=0.023\pm0.008$. The oxygen loss does not begin until 875 °C in argon, but oxygen reabsorption begins at temperatures as low as 600 °C, as previously observed.[6]

Figure 2 shows the Ce concentration dependence of the Meissner effect for samples prepared with the corresponding stoichiometric mixtures of starting materials and reduced in pure argon at 900 °C. A sharp maximum occurs in the apparent superconducting fraction at $x=0.15$, demonstrating our ability to carefully control the cation composition. To maximize the apparent superconducting fraction, the measurements presented here on the effect of the degree of reduction are performed on samples prepared with $x=0.15$.

After thinning to 125 μm, six Au contacts in a rectangular Hall bar pattern were evaporated onto the samples, then annealed for 1 hr at 300 °C under flowing argon, reducing the contact resistances to less than 1 ohm.[7] Hall effect and resistivity measurements were performed continuously as the temperature of the samples was slowly varied ($\approx$5 K/hr). The Hall voltage was measured using a 5-T magnet, with field reversal to eliminate the longitudinal resistance component. Spurious voltages arising from thermoelectric effects were eliminated using the ohmicity of the Hall voltage and current levels were checked for the absence of self-heating. Resistance measurements and Hall voltage measurements were made with two different pairs of contracts for each sample. After elimination of spurious voltages, the Hall voltages agree within the scatter of the data. The resistivities agree within 1–10 % between different pairs of contacts. The sample thicknesses are known to within 2%. No corrections were made for the packing fraction (81±1%), which is independent of the degree of reduction.

In Fig. 3(a) we show the superconducting critical temperatures, as determined from the onsets of the Meissner signal and the resistivity, for sintered pellets with $x=0.15$ annealed in pure argon at 930 °C (method 1) and in oxygen partial pressures $P(O_2)=5\times10^{-4}$, 10^{-2}, and 10^{-1} atm. at 1050 °C (method 2). In Fig. 3(b) we show the field

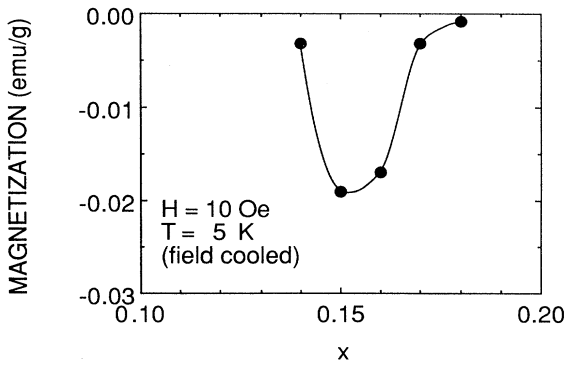

FIG. 2. Cerium concentration dependence (x) of the field-cooled (Meissner) magnetization in a field of 10 Oe at 5 K, for samples annealed in 99.9995% purity argon for 24 hr at 900 °C.

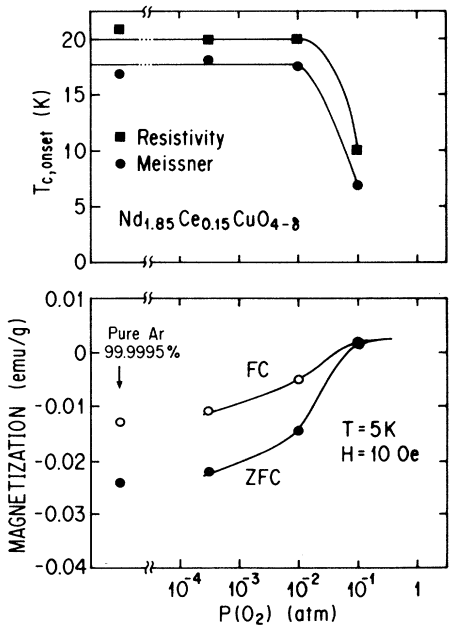

FIG. 3. $P(O_2)$ dependence of (a) T_c from magnetization and resistivity measurements and (b) the field cooled (FC) and zero-field cooled (ZFC) magnetization in a field of 10 Oe, for the samples on which the Hall effect was measured.

cooled (Meissner) and zero field cooled (shielding) magnetization in a field of 10 Oe for the same samples. The corresponding Meissner and shielding volume fractions at 5 K in an applied magnetic field of 10 Oe (without demagnetization corrections) for the sample reduced in pure argon are 12% and 24%, respectively.

Our TGA results indicate that only very small changes in δ occur with reduction. Surprisingly, however, large systematic changes occur in the apparent carrier density N as the degree of reduction is varied, as shown in Fig. 4. N has been calculated from the measured Hall coefficient R_H by use of the relation

$$N=(V_{\text{cell}}|R_H|e)^{-1}\ , \tag{1}$$

where N is in units of no./unit cell, R_H is in cm^3/C, V_{cell} is in cm^3, and $e=1.6\times10^{-19}$ C. Here, $V_{\text{cell}}=1.89\times10^{-22}\ \text{cm}^3$. The Hall coefficient is negative over the entire temperature range for all samples, in agreement with previous measurements on ceramics,[1] c-axis oriented thin films,[8] and measurements at 77 and 300 K on a single crystal[9] with H||c. At fixed temperature we find dramatic and systematic changes in N with degree of reduction of the reducing atmosphere. If we compare the variation in N with oxygen partial pressure at 100 K, we find that the measured value of N increases from 0.6 ± 0.05 carriers/unit cell for the most weakly reduced sample to 1.45 ± 0.10 carriers/unit cell for the most highly reduced sample. Measurement of the Hall coefficient at 100 K for $P(O_2)=5\times10^{-4}$ atm yields a value for N of approximately 1 carrier/unit cell (0.9 ± 0.15). A previous measurement of a ceramic $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$ sample annealed for 10 hr under Ar-O_2 gas mixture flow with an oxygen partial pressure of 1×10^{-4} atm found roughly 1.2 n-type carriers/ unit cell at 100 K, in close agreement with this work,[1] while measurement on a c-axis oriented epitaxial thin film found 2.0 n-type carriers/unit cell at 100 K.[8]

In the preceding discussion we have taken the value of the Hall coefficient to be that measured at 100 K. The linearly extrapolated values of the Hall coefficient at 0 K do not vary significantly from the 100-K values, and do not change our conclusions regarding the large change in Hall coefficient with degree of reduction. Comparison between our results and those on oriented thin films[8] suggests that averaging over any crystalline anisotropy may affect the degree of temperature dependence but does not change the sign of the Hall coefficient from that measured for magnetic fields normal to the Cu-O plane. We note that the large increase in Hall coefficient (and positive sign) with decreasing temperature below 80 K observed in one recent measurement of single crystals[10] of $Nd_{2-x}Ce_xCuO_{4-\delta}$ (x unspecified) is not clearly observed here, but more detailed measurements of the Hall coefficient near T_c are planned.

Our results for the temperature variation of the resistivity are shown in Fig. 5. Only the sample reduced under an oxygen partial pressure of 5×10^{-4} atm exhibits a

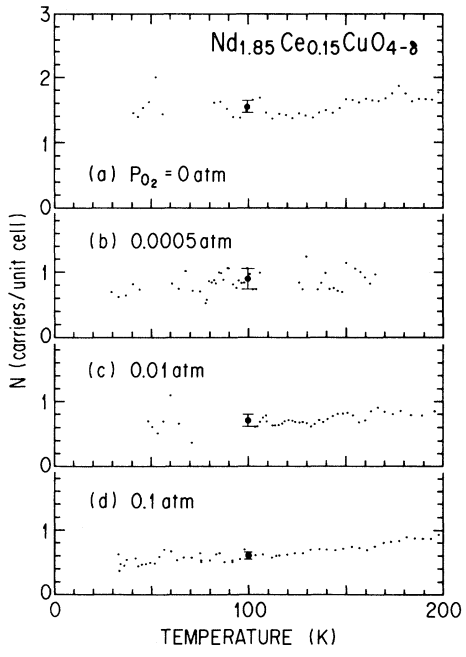

FIG. 4. Apparent carrier density versus temperature as a function of reducing atmosphere. (a) Oxygen partial pressure $P(O_2)=0$ atm, (b) $P(O_2)=5\times10^{-4}$ atm, (c) $P(O_2)=1\times10^{-2}$ atm, (d) $P(O_2)=1\times10^{-1}$ atm. Total pressure (oxygen plus argon) is 1 atm for all four cases. Symbols at 100 K mark interpolated values (and uncertainty) of carrier density used in text.

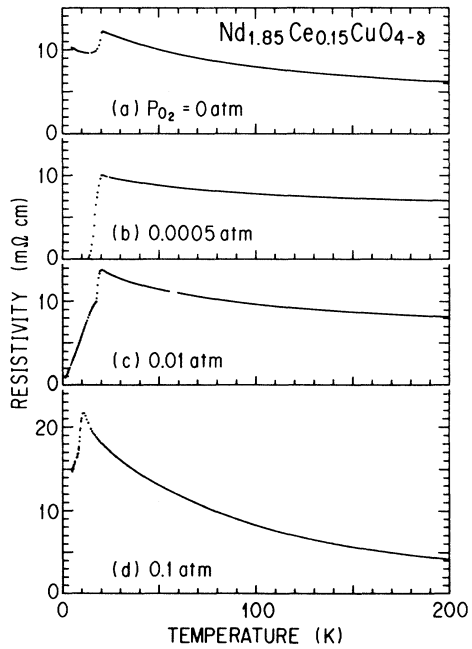

FIG. 5. Resistance versus temperature as a function of reducing atmosphere. (a) Oxygen partial pressure $P(O_2)=0$ atm, (b) $P(O_2)=5\times10^{-4}$ atm, (c) $P(O_2)=1\times10^{-2}$ atm, (d) $P(O_2)=1\times10^{-1}$ atm. Total pressure (oxygen plus argon) is 1 atm for all four cases.

zero resistance state (at temperatures above 4.2 K). As the degree of reduction is decreased from this value (increasing oxygen partial pressure), a shoulder develops below the 20-K superconducting onset, then the onset itself appears to shift to 10 K, as also seen in the Meissner data. For the most highly reduced sample (pure argon atmosphere), the superconducting onset remains at 20 K, but the sample no longer shows any indication of approaching a zero resistance state. A similar dependence of the resistivity below T_c has been reported[11] for a sample reduced in CO_2 for 1 hr at 900 °C. Interestingly, the residual resistivity disappeared for samples annealed at 1000 or 1100 °C, where partial sample decomposition occurs.

We now turn to a brief discussion of our results. If the physical effect of reduction is only to increase the number of carriers by 2δ, then much smaller changes in the Hall coefficient and apparent carrier density due to reduction might be expected. The anomalously large changes in the apparent carrier density could be due to the removal of oxygen atoms from "key sites" which when occupied, strongly suppress the mobile carrier density in the Cu-O planes. In fact, recent experimental work has shown that the oxygen atoms that are removed during heat treatment come from oxygen sites within the O_2 plane that separates CuO_2 planes or from interstitial apical oxygen sites not occupied in the perfect stoichiometric crystal.[6] The former possibility has been independently suggested on theoretical grounds.[12] X-ray absorption measurements[13] by some of us also imply a large increase in the electron density at the copper sites with increasing degree of reduction. An alternative explanation would be the presence of a very small number of highly mobile holes in addition to the majority electron carriers. Choosing between these alternatives will require (1) accurate knowledge of δ before reduction and the change in δ and the distribution of oxygen vacancies[14] (or excess oxygen atoms) for each degree of reduction or (2) independent evidence for a minority band of much higher mobility holes. Nevertheless, it is difficult to understand how an electron-hole two-band model could explain the observed variations in Meissner effect and resistivity with degree of reduction, while the "key site" model is consistent with all three experiments.

We also note that from the dependence of T_c on annealing temperature and duration for annealing in pure N_2, it has been suggested that a nonzero "critical oxygen comparison" is required to produce fully superconducting samples.[4] The experimentally observed difficulty in achieving zero resistance in single crystals, despite large Meissner fractions, has been attributed to either variations in local oxygen concentration or the presence of interstitial CuO flux.[4] Our observation of a zero resistance state and a large Meissner signal for a ceramic sample reduced under a nonzero "optimal" partial pressure of oxygen confirms that complete reduction is not required for bulk superconductivity and zero resistivity. Further, the absence of such a zero resistance state above 4.2 K in the most highly reduced sample indicates that even in the absence of the CuO flux used to grow single crystals, the achievement of zero resistance depends on the reducing conditions. While our results are consistent with the existence of large local variations in local oxygen concentration for non optimally reduced samples, the TGA results suggest that annealing after reduction at temperatures just below 600 K might reduce any inhomogeneities in the oxygen distribution and sharpen the resistive transitions.

In conclusion, we observe large, systematic changes in Meissner fraction, Hall coefficient, and resistivity with increasing degree of reduction at fixed cerium concentration for ceramic samples of $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$. These results call into question the quantitative values of thermodynamic and transport properties derived from experiments performed on samples of $Nd_{2-x}Ce_xCuO_{4-\delta}$ in which the effect of varying the degree of reduction was not systematically studied. Further understanding of the different physical roles of cerium doping and oxygen reduction in this material will require more precise determinations of δ before and after reduction and in the distribution of oxygen atoms and/or vacancies due to reduction.

Note added in proof. An extended discussion of the results reported in Ref. 10 for $Nd_{2-x}Ce_xCuO_{4-\delta}$ crystals has recently appeared.[15] In additional measurements on samples with $x=0.15$, 0.17, and 0.18, we find that for the Ce concentration that maximizes the relative Meissner fraction ($x=0.15$), the Hall coefficient is again negative at all temperatures. For higher Ce concentrations ($x=0.17$ and 0.18), we observe the same crossover to a positive Hall coefficient below 75 K and a strong low-temperature dependence seen in some of the data of Ref. 10. Details will be presented elsewhere.

We are happy to acknowledge contributions by T.R. Nichols at an early stage of this work and useful discussions with H. Oyanagi and K. Yamaji. N.A.F. acknowledges partial support from the Science and Technology Agency (Japan) and the National Science Foundation (USA).

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