Single-crystal neutron-diffraction structures of reduced and oxygenated Nd$_{2-x}$Ce$_x$CuO$_y$

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The structures of single crystals of oxygenated and reduced ($T_c=24$ K) Nd$_{1.85}$Ce$_{0.15}$CuO$_y$ ($y \approx 4$) were examined by neutron diffraction. Although refinements of various models including interstitial oxygen atoms was inconclusive, Fourier maps of the oxygenated crystal exhibit peaks at the apical O(3) oxygen site. This peak is almost entirely absent in the superconducting reduced crystal. These results are consistent with results from a previous study of oxygenated and reduced Nd$_2$CuO$_y$.

Nd$_{2-x}$Ce$_x$CuO$_y$ ($x \approx 0.15$, $y \approx 4$) (Refs. 1 and 2) is unusual among the cuprate superconductors for several reasons. Substitution of the rare earth with a tetravalent Ce^{4+} ion produces charge carriers which are believed to be electrons (n-type doping) rather than holes (p-type) as is the case for the majority of cuprate superconductors. The T' structure of Nd$_{2-x}$Ce$_x$CuO$_y$ (Fig. 1) consists of infinite square planar CuO$_2$ layers where the O(2) atoms lie in a plane sandwiched between Nd/Ce layers rather than in the apical Cu sites as in the T structure of La$_2$CuO$_4$. Superconductivity only occurs within a narrow composition range ($0.145 \leq x \leq 0.17$), and then only after reducing as-made samples in flowing inert gas. In this paper we will present the results of single-crystal neutron-diffraction investigations of possible structural differences between as-made and reduced Nd$_{1.85}$Ce$_{0.15}$CuO$_y$ ($T_c=24$ K).

The oxygen stoichiometry and possible changes in the stoichiometry during the reduction step have been extensively studied by iodometric titration and thermogravimetric analyses.[1–7] An interesting conclusion from these studies is that as x varies from 0 to 0.15, Δy in the reduction step varies from as much as ~0.07 at $x=0$ to values below the sensitivities of the measurement techniques (~0.01) at $x=0.15$. However, it must be emphasized that, although the amount of oxygen removed during the reduction step is very small, the reduction step is required to transform the material to the superconducting phase.

The first question that arises from these studies is whether there is partial oxygen atom occupancy of the apical site, O(3). We would also wish to know whether there are any changes in the occupancies of the oxygen atoms in the copper planes, O(1), and of those between the Nd(Ce) sheets, O(2), in going from the as-made to the reduced materials. A neutron powder diffraction study by Izumi *et al.*[8] of as-made (nonsuperconducting) and reduced (superconducting) material found no statistically significant differences between the two samples, with O(1) fully occupied and O(2) about 3% vacant. There is no mention of any attempt to analyze the

O(3) site. In another neutron powder diffraction study, Kwei *et al.*[9] examined the O(3) site and reported difference Fourier contours present in the as-made sample at the O(3) site that were absent in the reduced sample. Nevertheless, attempts to refine the occupancies led to values of essentially zero. Finally, positive evidence for the occupancy of the apical oxygen site was obtained in a Mössbauer study of Nd$_{2-x}$Ce$_x$CuO$_y$ doped with small amounts of ^{57}Co in the Cu sites in which the presence of 5 and 6 coordinate Co species was detected.[10] However, it is feasible that the oxygen coordination of cobalt and copper sites are not the same.

Recently, we reported a single-crystal neutron-diffraction study of oxygenated and reduced Nd$_2$CuO$_y$ ($x=0$).[11] The occupancy of the apical oxygen site was ~0.10 (per formula unit) for the oxygenated sample and ~0.04 for the reduced sample. Although these values are expected to be much smaller for the case with $x=0.15$, in this paper we report the results of a similar study on single crystals of Nd$_{1.85}$Ce$_{0.15}$CuO$_y$.

Single crystals of Nd$_{1.85}$Ce$_{0.15}$CuO$_y$ were grown by a flux
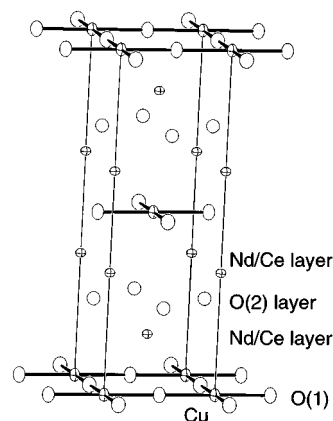

FIG. 1. The single-crystal neutron-diffraction structure of Nd$_{1.85}$Ce$_{0.15}$CuO$_y$ at 15 K derived from model 1.

TABLE I. Lattice constants at 15 K and experimental parameters for the single-crystal neutron-diffraction data collection on oxygenated and reduced $Nd_{1.85}Ce_{0.15}CuO_y$

	Oxygenated	Reduced
$a=b$ (Å)	3.9108(9)	3.9075(9)
c (Å)	11.958(3)	11.945(4)
V (Å^3)	182.89(8)	182.38(9)
Temperature (K)	15	15
Number of histograms	16	14
Total number of reflections, $I>3\sigma(I)$	454	390

method as previously described.[12] Two nearly identical plate-like crystals of dimensions $5\times2.5\times\sim0.05$ mm^3 were selected for the experiment. The oxygenated (nonsuperconducting) crystal was annealed in pure oxygen at 950 °C for 24 h, and then slowly cooled for 48 h to room temperature. The reduced (superconducting) crystal was annealed in pure nitrogen at 900 °C for 24 h, followed by cooling to room temperature over a period of 5 h. A measurement of the Meissner effect shows a T_c onset of 24 K.

Single-crystal neutron-diffraction data were obtained using the time-of-flight single-crystal diffractometer[13] (SCD) at IPNS with the sample at 15 K. The SCD is equipped with a large area (30×30 cm^2) position-sensitive detector, a Huber crystal orienter, and a closed-cycle helium refrigerator. With a stationary crystal and detector, a three-dimensional histogram of a portion of reciprocal space is obtained. For this study, 14 histograms with the crystal in different orientations were collected so that more than one octant of reciprocal space was covered. The lattice constants and experimental parameters are given in Table I. Details of the peak integration, data reduction, and structure refinement procedures and programs have been provided previously.[14]

In all the refinements a scattering length of $(1.85b_{Nd} + 0.15b_{Ce})/2$ was used for the atom on the Nd/Ce site. A secondary extinction correction was included and all atoms except O(3) were refined with anisotropic temperature factors. For O(3), the isotropic temperature factor was not refined. The final structural parameters are given in Table II.

Model 1 refers to the structures of oxygenated and reduced $Nd_{1.85}Ce_{0.15}CuO_y$ without any apical O(3) oxygen atoms. The results of the model 1 refinements yields an oxygen stoichiometry of 3.92(3) (per Cu atom) for the oxygenated crystal and 3.95(3) for the reduced. Although the relative values are the opposite of what would be expected, the difference of 0.03(4) is less than one standard deviation and therefore is not statistically significant.

Based on a refinement of model 1, the largest positive peak in the difference Fourier of the oxygenated crystal occurs at $[0,0,\sim0.2]$, which the is apical oxygen site in the La_2CuO_4-type T structure. A contour plot of the difference Fourier for the $y=0$ plane is shown in Fig. 2(a).

Including an oxygen atom at the O(3) site is referred to as model 2. Refinement of the O(3) site occupancy in model 2 of the oxygenated crystal leads to 0.06(1) apical oxygen atoms per Cu atom and an overall stoichiometry of 3.95(3).

TABLE II. Structural parameters and interatomic distances for oxygenated and reduced $Nd_{1.85}Ce_{0.15}CuO_y$ at 15 K. Space group $I4/mmm$. The atomic positions are Nd/Ce $4e[0,0,z]$; Cu $2a[0,0,0]$; O(1) $4c[1/2,0,0]$; O(2) $4d[0,1/2,1/4]$; O(3) $4e[0,0,z]$. Occupancies (n) are expressed in terms of atoms per formula unit.

	Model 1		Model 2	
	Oxygenated	Reduced	Oxygenated	Reduced
Nd/Ce n	2	2	2	2
z	0.35277(7)	0.35276(7)	0.35268(6)	0.35272(7)
U_{11} (Å^2)	0.0033(3)	0.0030(3)	0.0032(3)	0.0031(3)
U_{33} (Å^2)	0.0024(3)	0.0029(3)	0.0021(3)	0.0028(3)
Cu n	1	1	1	1
U_{11} (Å^2)	0.0033(3)	0.0039(3)	0.0033(3)	0.0039(3)
U_{33} (Å^2)	0.0057(4)	0.0056(4)	0.0056(4)	0.0055(4)
O(1) n	1.97(2)	1.97(2)	1.96(2)	1.96(2)
U_{11} (Å^2)	0.0046(5)	0.0050(5)	0.0043(5)	0.0050(5)
U_{22} (Å^2)	0.0065(5)	0.0075(5)	0.0061(5)	0.0074(5)
U_{33} (Å^2)	0.0082(4)	0.0078(5)	0.0081(4)	0.0077(5)
O(2) n	1.95(2)	1.98(2)	1.93(2)	1.96(2)
U_{11} (Å^2)	0.0055(4)	0.0055(4)	0.0053(4)	0.0055(4)
U_{33} (Å^2)	0.0059(4)	0.0070(5)	0.0056(4)	0.0068(5)
O(3) n	0	0	0.06(1)	0.04(1)
z			0.193(2)	0.196(4)
U_{iso} (Å^2)			0.005	0.005
y	3.92(3)	3.95(3)	3.95(3)	3.96(3)
$R(F)$	0.0495	0.0471	0.0479	0.0472
$wR(F)$	0.0463	0.0471	0.0446	0.0462
Reduced χ^2	1.4171	1.4465	1.3737	1.4242
Nd/Ce-O(1) (Å)	2.6312(7)	2.6288(4)	2.6319(7)	2.6291(7)
Nd/Ce-O(2) (Å)	2.3095(6)	2.3073(6)	2.3089(6)	2.3071(7)
Nd/Ce-O(3) (Å)			1.91(3)	1.87(5)
Cu-O(1) (Å)	1.9554(4)	1.9538(4)	1.9554(4)	1.9538(4)
Cu-O(3) (Å)			2.30(3)	2.34(5)

The reason for the negative trough in Fig. 2(a) is not known, but may be indicative of anharmonicity in both the O(3) site and the nearby Nd/Ce site, possibly resulting from the short (N/Ce)-O(3) contact of 1.91(3) Å.

There is some question as to whether a Nd-O distance of ~1.9 Å is chemically reasonable. Pauling[15] gives crystal radii of 1.08 Å for Nd^{3+}, 1.01 Å for Ce^{4+}, and 1.40 Å for O^{2-}. This latter value is also the van der Waals radius of oxygen. The covalent radius of oxygen is given as 0.66 Å. Since O(3) would be strongly covalently bonded to copper, it is possible it would have a smaller effective negative charge and therefore a smaller ionic radius, permitting closer contact with Nd^{3+}. Other possibilities are that the occupancy of the O(3) site produces a distortion of the lattice or requires a vacant Nd/Ce site. Although we cannot rule out these possibilities, the Nd/Ce occupancy parameter did not deviate significantly from full occupancy.

In the case of the reduced crystal, the difference Fourier after refinement of model 1 is virtually featureless, as shown in Fig. 2(b). However, for purposes of comparison, an oxygen atom placed at the O(3) site in the reduced crystal led to a refined occupancy of 0.04(1) per Cu atom. It should be
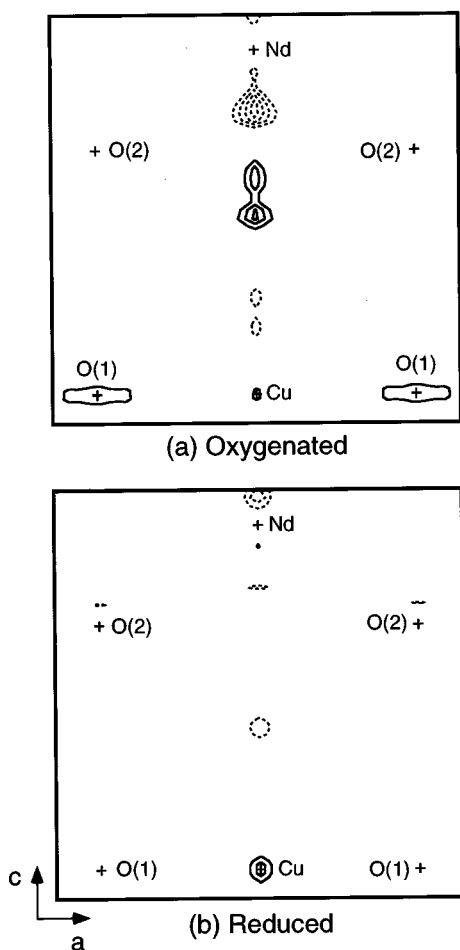
FIG. 2. Difference Fourier contours of (a) oxygenated and (b) reduced $Nd_{1.85}Ce_{0.15}CuO_y$ following refinement of model 1. Positive density contours are drawn with solid lines and negative contours are drawn with dashed lines. Contour level steps are approximately 1% of the peak heights of O(1) and O(2) in the Fourier synthesis.

annealing in a reducing atmosphere, even though the amount of oxygen which is removed is minuscule. Decreasing the cerium content leads to an increase in the amount of oxygen removed during reduction, although $Nd_{1.85}Ce_{0.15}CuO_y$ does not become superconducting for $x < 0.14$. The largest change in oxygen content, as much as $\Delta y \approx 0.07$ from TGA measurements, occurs in Nd_2CuO_y. Our previous single-crystal neutron study of oxygenated and reduced Nd_2CuO_y yielded $\Delta y = 0.08(5)$, with 0.10(2) and 0.04(1), respectively, O(3) atoms per formula unit.

For $Nd_{1.85}Ce_{0.15}CuO_y$, the change in y has been shown from TGA measurements to be ~ 0.01, which is at or less than the precision of most diffraction experiments. Thus, it is not surprising that the results of the refinements are inconclusive. However, the difference Fourier of the oxygenated crystal shows a peak at the apical oxygen site. The peak is clearly absent in the difference Fourier of the reduced crystal. These same observations are reported for a neutron *powder* diffraction study of oxygenated and reduced $Nd_{1.85}Ce_{0.15}CuO_y$.[9] Furthermore, the Mössbauer study of $Nd_{1.85}Ce_{0.15}Cu(^{57}Co)O_y$ provides evidence for the existence of apical oxygen atoms, although it is possible that the coordination of the Co and Cu sites are different.[10] However, from the consistency of these observations, it appears that the apical oxygen site may be partially occupied in oxygenated $Nd_{1.85}Ce_{0.15}CuO_y$, and that the occupancy decreases in the reduction step to produce the superconducting material. In the case of nonsuperconducting Nd_2CuO_y where the changes are greater, the evidence for this is convincing.[11] The O(1) and O(2) sites appear to be slightly less than fully occupied in both the oxygenated and reduced crystals of $Nd_{1.85}Ce_{0.15} CuO_y$, but any changes at these sites between the two crystals is not statistically significant within standard deviations of $\sim 1\%$.

noted that in the case of Nd_2CuO_y, the O(3) occupancy of the reduced crystal was also 0.04(1).[11]

Much of the interest in $Nd_{1.85}Ce_{0.15}CuO_y$ is derived from the observation that it only becomes superconducting after

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