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Evidence of apical oxygen in Nd_2CuO_y determined by single-crystal neutron diffraction

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The defect structure of oxygenated and reduced Nd_2CuO_y $(y \approx 4)$ was investigated by single-crystal neutron diffraction. Structural refinements indicate the presence of interstitial oxygen atoms in the "apical" O(3) position, directly above or below the copper atoms. The occupancy of the apical oxygen site is ~ 0.10 (per formula unit) for the oxygenated sample and ~ 0.04 for the reduced one. Both the in-plane O(1) and the out-of-plane O(2) oxygen sites were found to be deficient, but their occupancy did not vary, within the error bars, between the two crystals. The difference in oxygen content between the two crystals, as calculated from the structural refinements, is consistent, within the error bars, with the thermogravimetric analysis values reported in the literature.

INTRODUCTION

The family of cuprates based on the T' structure, M_2CuO_y $(M = \mathrm{Nd, Pr, Sm, Eu};\ y \approx 4)$, has been the subject of considerable research effort in recent years. Superconductivity, with T_c up to 24 K, is induced in these compounds by partially replacing the rare earth with a tetravalent ion (such as Ce^{+4}).[1–4] This substitution dopes the CuO_2 layers with charge carriers, which, unlike the majority of the other cuprate superconductors, are believed to be electrons (n-type doping) rather than holes (p-type). The superconducting phase diagram of $Nd_{2-x}Ce_xCuO_y$ is quite different from the one displayed by most of the p-type cuprate compounds. For $Nd_{2-x}Ce_xCuO_{6y}$, superconductivity is found in the composition range $(0.145 \leq x \leq 0.18)$, and only after as-made samples are reduced, usually at $\sim 900\,^{\circ}\mathrm{C}$ in flowing inert gas.[2] For $x < 0.145$ the compound is an antiferromagnetic insulator, while $x \approx 0.2$ is the solubility limit of Ce in the compound. The superconducting critical temperature T_c has its maximum value when superconductivity appears. T_c remains constant for $0.15 \leq x \leq 0.165$, and decreases thereafter.

Measurements of the superconducting phase fraction by magnetic techniques indicate that bulk superconductivity exists only in a very narrow range of compositions $(\Delta x \approx 0.01)$, centered at $x \approx 0.15–0.17$ (different laboratories report slightly different values for the optimum composition).[1–4,5–7] Studies have shown that, for samples with the optimum cerium content, both the critical temperature and the superconducting phase fraction can be varied by changing the oxygen partial pressure during the reduction step.[8,9] Reduction near the decomposition point yields samples with the best superconducting properties. However, for most powder samples, the shielding fraction never exceeds 30%. The exact role of the reduction step has never been completely clarified. The amount of oxygen Δy removed during this processing step is very small (the reported value varies between 0.01 and 0.04 oxygen atoms per formula unit[5,9–12]). An equivalent optimally doped condition cannot be achieved at other combinations of oxygen reduction and cerium substitution.[13] These two features of the behavior suggest that the oxygen defect whose concentration is changed by reduction has a dramatic effect on the superconducting properties.

Many groups have investigated the behavior of the oxygen content as a function of cerium content and processing conditions, using thermogravimetric analysis (TGA) and idometric titration. These studies are particularly difficult, since the variations in oxygen stoichiometry are very small, especially for samples near optimum doping. There is general consensus on the observation that the amount of oxygen Δy that can be removed by the reduction step is maximum for $x = 0$ $(\Delta y \approx 0.7)$ and decreases as a function of x.[5,9,11,12,14,15] However, the total oxygen content of samples processed under specific thermodynamic conditions, and its behavior as a function of x, are still the subject of considerable controversy. A few studies have concluded that the oxygen content of all samples is $y \leq 4$, and that samples slowly cooled in pure oxygen are essentially stoichiometric $(y \approx 4)$ for all values of x.[9,12] Other groups have concluded that oxygen-annealed samples have $y > 4$, and have suggested the existence of interstitial oxygen atoms.[5,14,15]

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Neutron diffraction is the most sensitive technique for investigating the occupancy of oxygen sites as well as the presence of interstitial oxygen atoms. However, neutron powder diffraction studies have so far failed to give a clear picture of the oxygen defect structure in $Nd_{2-x}Ce_xCuO_y$, or to determine which oxygen site is variable between reduced and as-made samples. In most cases,[11,16,17] small amounts of oxygen vacancies are detected on both the planar site [O(1)] and the out-of-plane site [O(2)] of the *T′* structure (Fig. 1). However, the deviations from full occupancy are at best a few standard deviations and could easily be influenced by improper modeling of the oxygen displacements (e.g., the use of a harmonic model for thermal vibrations that are actually anharmonic). In addition, when as-made (nonsuperconducting) and reduced (superconducting) samples of optimally doped $Nd_{2-x}Ce_xCuO_y$ were compared using neutron powder diffraction, no significant differences in the occupancies of O(1) and O(2) were detected.[16,17] In a neutron powder diffraction study of an as-made $Nd_{1.85}Ce_{0.15}CuO_y$ powder sample,[17] Kwei and co-workers reported the observation of above-background density in the Fourier difference map at the "apical oxygen" position O(3). This feature was absent for a reduced sample with the same metal-ion stoichiometry. However, the authors were unable to detect significant amounts of apical oxygen in their Rietveld refinements for either sample and, thus, were not able to make a convincing case for the existence of apical oxygen defects.

Refinements of single-crystal neutron-diffraction data should be, in principle, more sensitive than powder methods to defects occurring in small concentrations, due to the reduced correlation between structural parameters. Clearly, the question relevant to superconductivity concerns the nature of oxygen interstitial or vacancy defects in the Ce-substituted compound. However, the difference in oxygen content between superconducting and nonsuperconducting samples is so small that detection by diffraction methods will be very difficult. Therefore, as a preliminary step, we have chosen to study the oxygen defect structure in oxidized and reduced samples of Nd_2CuO_y, where Δy is much larger.

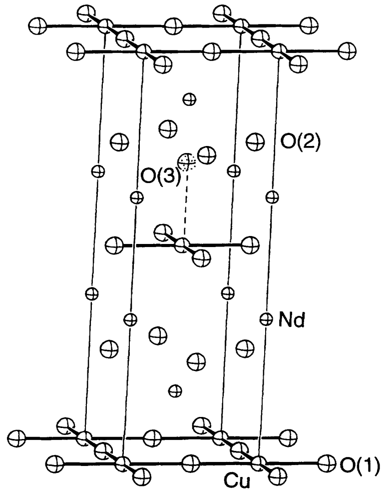

FIG. 1. Crystal structure of Nd_2CuO_y. O(3) is a defect site in the "apical" position, which we determined to have variable concentration (see text). Since the defect site occupancy is small and the defect may not obey the symmetry of the host lattice, its symmetry equivalent sites are not shown.

Recently, Marin and co-workers presented a single-crystal neutron-diffraction study on a Nd_2CuO_y single crystal, in both oxidized and reduced states.[18] They found both the O(1) and O(2) sites to be approximately 2.5% deficient in the reduced state. After oxygenation, the occupancy of O(2) remained the same, while O(1) became fully occupied. No oxygen in the apical position was detected in this study. Marin and co-workers collected data at room temperature on the Siloé reactor source; the maximum value of the transferred momentum in their experiment was $q = 8.4$ Å^{-1}.

In this study we present the results of a similar experiment, performed on nitrogen reduced and fully oxygenated Nd_2CuO_y single crystals. The data were collected at 15 K on a spallation source, which allows an extended q range ($q \leq 17.5$). Intensity in the difference Fourier maps at the apical oxygen position was detected for both samples, with the density peak having a higher intensity for the oxygen-annealed crystal. Structural refinements based on the single-crystal neutron-diffraction data indicate that the occupancy of the apical oxygen site, O(3), is ~ 0.10 for the oxygenated sample and ~ 0.04 for the reduced one. Both O(1) and O(2) were found to be deficient, but their occupancies do not vary, within the error bars, between the two crystals. The value of Δy, as calculated from the structural refinements, is consistent, within the error bars, with the TGA values reported in the literature.

EXPERIMENTAL

Single crystals of Nd_2CuO_y were grown by a flux method as previously described.[19] Two nearly identical platelike crystals of dimensions $3 \times 3 \times 0.06$ mm^3 were selected for the experiment. Crystal no. 1 was annealed in pure oxygen at 950 °C for 24 h, and then slowly cooled for 48 h to room temperature. Crystal no. 2 was annealed in pure nitrogen at 900 °C for 24 h, followed by cooling to room temperature over a period of 5 h. Single-crystal neutron-diffraction data were collected on both samples at 15 K, using the time-of-flight single-crystal diffractometer (SCD) at IPNS, equipped with a large-area (30×30cm^2) position-sensitive detector and a closed-cycle refrigerator.[20] The crystals were mounted at the end of an aluminum pin using low-temperature adhesive. With a stationary crystal and detector, a three-dimensional histogram of a portion of reciprocal space is obtained. For this study, 14 histograms were collected, with the crystal in different orientations, so that more than an octant of reciprocal space was covered. The experimental parameters for the measurements are given in Table I. Integrated intensities of Bragg reflections were obtained using the IPNS-SCD single-crystal analysis package.[21] Structure refinements were performed using a multiwavelength program (ANVLS) based on ORFLS.[22]

TABLE I. Lattice constants at 15 K and experimental parameters for the single-crystal neutron-diffraction data acquisition on oxygenated and reduced Nd_2CuO_y samples.

	Oxygenated	Reduced
Cell determination		
$a=b$ (Å)	3.9370(7)	3.9327(10)
c (Å)	12.139(3)	12.132(3)
c/a	3.0833(3)	3.0849(4)
Measurements		
Temperature (K)	15	15
Number of reflections	843	682
Number of histograms	14	14
q-range (Å^{-1})	$2.92 \le q \ge 17.5$	$2.92 \le q \ge 17.5$

STRUCTURAL REFINEMENTS

Refinements of the structural parameters were carried out in the $I4/mmm$ space group. Integrated intensities were corrected for the wavelength-dependent incident flux, detector efficiency, and absorption, using a polyhedral model based on the actual dimensions of the crystals. The full data sets consisted of 14 separate histograms, with partial overlapping. The scale factor of each histogram and a Zachariasen type-I overall isotropic extinction parameter were included among the refined parameters. Scattering lengths used were $b(\mathrm{Nd})=0.769$, $b(\mathrm{Cu})=0.7718$, and $b(\mathrm{O})=0.5803$. Preliminary sets of refinements were carried out using Nd, Cu, O(1), and O(2) only. The occupancies of Nd and Cu were set to their full values, while the occupancies of the oxygen atoms were refined. Anisotropic temperature factors were used for all the atoms. Fourier difference contour maps were constructed using observed and calculated structure factors. A scattering density peak at approximately [0,0,0.2] is present in the maps from both data sets, and is the strongest peak in the difference maps. The peak for the oxygenated crystal is about three times as high as for the reduced crystal. On the basis of these observations, new refinements were carried out using a structural model that included an apical oxygen atom O(3). The O(3) position was initially set at [0,0,0.2], and its z coordinate and occupancy were included among the refined parameters. The O(3) thermal displacement was modeled using an isotropic temperature factor (u_{iso}). For the reduced crystal, u_{iso}[O(3)] was fixed at a reasonable value. For the oxygenated crystal, u_{iso} could be refined, although the uncertainty on this parameter is quite large. The refinement of u_{iso}[O(3)] (or the fixed value chosen for the reduced-crystal refinement) produces no significant change in the refined occupancy of O(3). The structural parameters refined using this model for both oxygenated and reduced crystals are reported in Table II.

The structural refinements clearly indicate that, for the oxygenated crystal, a significant amount of oxygen (~ 0.1 atoms/formula unit) is present in the O(3) "apical" position [0,0,z] ($z \approx 0.2$). Approximately 60% of these atoms are removed by the reduction process. The refined Cu-O(3) distances [2.45(2) and 2.49(5) for the oxygenated and reduced crystals, respectively] are comparable with typical copper–apical-oxygen distances for other cuprate superconductors. Oxygen vacancies are present on the O(2) (out-of-plane) site and, to a lesser extent, on the O(1) (in-plane) site. No change is observed for the O(2) occupancy upon reduction; the change in n[O(1)], although consistent with an increase in vacancy concentration, is less than one error bar.

In order to test the statistical significance of our model, Hamilton's ratio tests were performed.[23] First, the R factors of refinements based on an "ideal" model without interstitial oxygen or vacancies (model 1) were obtained for both crystals. Subsequently, models of increasing complexity were tested for significance using the Hamilton criterion. Model 2 includes oxygen atoms in the O(3) position. In model 3, the concentration of vacancies in the O(2) position is also refined. In model 4, the occupancies of both O(1) and O(2) are refined, while n [O(3)] is fixed to

TABLE II. Refined structural parameters from single-crystal neutron diffraction on oxygenated and reduced Nd_2CuO_y samples at 15 K. The atomic positions are: Nd $4e[0,0,z]$; 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. The occupancies of Nd and Cu were set to the ideal values. Numbers in parenthesis indicate statistical errors of the last significant digit. When the error is absent, the parameter is not refined.

	Oxygenated	Reduced
Nd		
z	0.35130(8)	0.35157(7)
n	2	2
$u_{11}=u_{22}$ (Å^2)	0.0007(2)	0.0021(2)
u_{33} (Å)	0.0016(3)	0.0025(2)
$u_{12}=u_{13}=u_{23}$ (Å^2)	0	0
Cu		
n	1	1
$u_{11}=u_{22}$ (Å^2)	0.0022(3)	0.0030(3)
u_{33} (Å^2)	0.0039(4)	0.0046(3)
$u_{12}=u_{13}=u_{23}$ (Å^2)	0	0
O(1)		
n	1.96(3)	1.94(2)
u_{11} (Å^2)	0.0022(5)	0.0032(4)
u_{22} (Å^2)	0.0057(5)	0.0052(5)
u_{33} (Å^2)	0.0058(4)	0.0061(4)
$u_{12}=u_{13}=u_{23}$ (Å^2)	0	0
O(2)		
n	1.91(2)	1.91(2)
$u_{11}=u_{22}$ (Å^2)	0.0027(3)	0.0038(3)
u_{33} (Å^2)	0.0041(4)	0.0053(4)
$u_{12}=u_{13}=u_{23}$ (Å^2)	0	0
O(3)		
z	0.202(2)	0.205(4)
n	0.10(2)	0.04(1)
u_{iso} (Å^2)	0.002(4)	0.003
$R(F)$	7.2%	6.44%
$R(F^2)$	13.07%	11.66%
wR	7.57%	7.06%
χ^2	1.6909	1.9722

TABLE III. Selected structural parameters from single-crystal neutron diffraction on oxygenated and reduced Nd_2CuO_y samples at 15 K, obtained using different structural models (see text).

	Oxygenated	Reduced
Model 1		
n[O(1)]	2	2
n[O(2)]	2	2
n[O(3)]	0	0
z[O(3)]		
$u_{\rm iso}$[O(3)] (Å^2)		
No. of parameters	25	25
$R(F)$	7.53%	6.56%
$R(F^2)$	13.63%	11.81%
wR	7.90%	7.19%
χ^2	1.7592	2.0022
Model 2		
n[O(1)]	2	2
n[O(2)]	2	2
n[O(3)]	0.09(2)	0.03(1)
z[O(3)]	0.202(2)	0.205(4)
$u_{\rm iso}$[O(3)] (Å^2)	0.001(4)	0.003
No. of parameters	28	27
$R(F)$	7.21%	6.50%
$R(F^2)$	13.13%	11.76%
wR	7.64%	7.14%
χ^2	1.7030	1.9917
Model 3		
n[O(1)]	2	2
n[O(2)]	1.93(2)	1.94(2)
n[O(3)]	0.11(2)	0.04(1)
z[O(3)]	0.202(2)	0.204(4)
$u_{\rm iso}$[O(3)] (Å^2)	0.003(4)	0.003
No. of parameters	29	28
$R(F)$	7.22%	6.46%
$R(F^2)$	13.12%	11.69%
wR	7.58%	7.10%
χ^2	1.6919	1.9811
Model 4		
n[O(1)]	1.95(3)	1.94(2)
n[O(2)]	1.94(3)	1.93(2)
n[O(3)]	0	0
z[O(3)]		
$u_{\rm iso}$[O(3)] (Å^2)		
No. of parameters	27	27
$R(F)$	7.52%	6.53%
$R(F^2)$	13.58%	11.76%
wR	7.88%	7.13%
χ^2	1.7558	1.9887
Model 5 (final)		
n[O(1)]	1.96(2)	1.94(2)
n[O(2)]	1.90(2)	1.91(2)
n[O(3)]	0.10(2)	0.04(1)
z[O(3)]	0.202(3)	0.205(4)
$u_{\rm iso}$ [O(3)] (Å^2)	0.003(4)	0.003
No. of parameters	30	29
$R(F)$	7.20%	6.44%
$R(F^2)$	13.07%	11.66%
wR	7.57%	7.06%
χ^2	1.6909	1.9722

TABLE IV. Results of Hamilton significance tests on the structural models presented in Table III. For models that differ only by the addition of one or more variables, the ratios of the weighed R values and the significance points α are given.

	Oxygenated	Reduced
Model 2 vs model 1		
wR_1/wR_2	1.0957	1.0070
Significance point α	$\alpha<0.005$	$\alpha\approx0.01$
Model 3 vs model 2		
wR_2/wR_3	1.0079	1.0056
Significance point α	$\alpha<0.005$	$\alpha\approx0.01$
Model 4 vs model 1		
wR_1/wR_4	1.0025	1.0084
Significance point α	$\alpha\approx0.1$	$\alpha\approx0.01$
Model 5 vs model 3		
wR_3/wR_5	1.0013	1.0057
Significance point α	$\alpha\approx0.20$	$\alpha\approx0.01$
Model 5 vs model 4		
wR_4/wR_5	1.0410	1.0099
Significance point α	$\alpha<0.005$	$\alpha<0.005$

zero. Model 5 is equivalent to the one reported in Table II, where all the occupancies are refined. Selected structural parameters for the five models are reported in Table III. In Table IV, the R factors of the five models are compared using the Hamilton criterion. For models that differ only by the addition of one or more variables, a significance point α is given, where α is the probability that the model with fewer parameters is correct. The confidence level can be calculated by the formula $CL=(1-\alpha)\times100$. For the oxygenated crystal, both the introduction of interstitial oxygen atoms in the O(3) position (model 2 vs model 1) and vacancies in the O(2) position (model 3 vs model 2) have better than 99.95% confidence, while vacancies on the O(1) position (model 5 vs model 3) are only at 80% confidence. For the reduced crystal, each model has approximately 99.9% confidence over the previous one. The confidence level of model 5 (where all the occupancies are varied) over model 4 (where only n[O(1)] and n[O(2)] are varied) is better than 99.95% for both crystals. From the Hamilton's ratio tests we conclude that apical oxygen atoms and vacancies on the O(2) sites are certainly present for both oxygenated and reduced crystals. Oxygen vacancies on the O(1) site are also likely to be present for both crystals, but the model without O(1) vacancies has significant probability ($\sim$20%) for the oxygenated crystal.

DISCUSSION

The present study has established, with a high degree of statistical confidence, the coexistence of oxygen interstitials [in the O(3) "apical" position] and oxygen vacancies [in the out-of-plane O(2) position and possibly in the O(1) in-plane position] for both oxygenated and reduced Nd_2CuO_y single crystals. The main difference between the two crystals is the decrease by 60% in the number of apical oxygen atoms upon reduction. From structure refinements, the total oxygen content of the two crystals is 3.97(4) and 3.89(3). The difference in oxygen content between the two crystals [0.08(5)] is consistent, within the error bars, with the values of Δy reported in the literature, based on iodometric titration and TGA. In a study very similar to ours, Marin and co-workers found no evidence of oxygen atoms in the apical position, and attributed the change in total oxygen content between oxygenated and reduced samples to a variation of the occupancy of the O(1) in-plane site.[18] We speculate that the extended q range of our measurement ($q_{\max}=17.5$ Å^{-1} for SCD vs $q_{\max}=8.4$ Å^{-1} for the instrument used by Marin and co-workers), as well as the fact that we collected data at low temperature, enabled us to better decorrelate occupancies from thermal parameters, and therefore enhanced our sensitivity for the low-concentration O(3) defect.

The simultaneous presence of interstitial oxygen atoms and oxygen vacancies would indicate that the defect structure of Nd_2CuO_y is much more complex than previously thought, and that this aspect of the crystal structure needs to be carefully considered for the Ce-doped material as well. The effects of cerium doping on the oxygen-defect structure of Nd_2CuO_y are presently unknown. The present work, however, suggests that a complex oxygen-defect structure needs to be considered as a possible explanation for the unusual superconducting phase diagram of $Nd_{2-x}Ce_xCuO_y$. For example, it is tempting to speculate that Ce substitution reduces the concentration of apical oxygen defects and the absence of these defects is necessary for superconductivity. Given the very small difference in total oxygen content between oxygenated and reduced samples of the Ce-substituted compound, and the errors bars for the occupancy of the apical O(3) site obtained in the present study, an analogous study of Ce-substituted crystals may not yield definitive results. However, such a study should be attempted.

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