Title

Structure and oxygen stoichiometry for the electron-doped cuprate superconductor Nd1.85Ce0.15CuO4-δ

Permalink

https://escholarship.org/uc/item/31s429h9

Journal

Physical Review B, 40(13)

ISSN

2469-9950

Authors

Kwei, GH
Cheong, S-W
Fisk, Z
et al.

Publication Date

1989-11-01

DOI

10.1103/physrevb.40.9370

Copyright Information

Peer reviewed

Structure and oxygen stoichiometry for the electron-doped cuprate superconductor $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$

G. H. Kwei, S-W. Cheong, Z. Fisk, F. H. Garzon, J. A. Goldstone, and J. D. Thompson
Los Alamos National Laboratory, Los Alamos, New Mexico 87545
(Received 4 August 1989; revised manuscript received 5 September 1989)

We have determined the structure of the newly discovered electron-doped superconductor $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$ at 11 and 300 K using high-resolution neutron-powder-diffraction techniques. Both nonsuperconducting oxygenated and superconducting Zr-gettered ($T_c \approx 24$ K with shielding and Meissner fractions of 30 and 16% at 5 K, respectively) samples were investigated to study the effect of Zr gettering on the crystal structure and oxygen stoichiometry. We find that the structure remains tetragonal ($I4/mmm$), with no evidence for Nd/Ce ordering, for both samples at both temperatures. Structure and oxygen stoichiometry of the oxygenated and Zr-gettered samples remain remarkably similar at both temperatures, the only difference being a slight decrease (but greater than three standard deviations) in the thermal parameters of the rare-earth ions along the c axis for the superconducting sample. Thermogravimetric analyses confirm the oxygen stoichiometry determined from the structural refinements.

The recent discovery by Tokura, Takagi, and Uchida[1] of the electron-doped cuprate superconductors, $Ln_{2-x}Ce_xCuO_{4-\delta}$ (with Ln = Pr, Nd, and Sm), in which tetravalent Ce has been doped into a trivalent lanthanide site, has presented the need for a better characterization of the normal and superconducting states of these materials and the opportunity to test the existing theories of superconductivity. Tokura *et al.*[1] showed that the structure of these compounds is similar to the undoped parent compound Nd_2CuO_4, which has the $I4/mmm$ tetragonal T' phase structure in which the copper ions are square-planar coordinated by oxygen ions.[2] Charge carriers in these materials appear to be electrons since both the Hall[1,3] and Seebeck[3,4] coefficients were found to be negative. They also used iodometric titrations to show that annealing in a low O_2 partial pressure, which enhances the bulk superconductivity, produces oxygen vacancies. Since then, Tranquada *et al.*[5] have used x-ray absorption near-edge spectroscopy (XANES) to show that the electrons introduced by Ce doping fill Cu $3d$ holes to produce Cu^+ ions.

These materials are not superconducting as prepared. Unlike the hole-doped cuprate superconductors, where annealing in an oxygen atmosphere following sintering is necessary, these materials must be annealed in a reducing atmosphere containing a low oxygen partial pressure or in a vacuum. Moran *et al.*[6] determined the oxygen stoichiometry of Ce-doped Pr_2CuO_4 and Nd_2CuO_4 as a function of Ce content and found that the oxygen stoichiometry decreases from 4.05 to 4.03 for $Nd_{2-x}Ce_xCuO_{4-\delta}$ as x is decreased from 0.15 to 0. Izumi *et al.*[7] have recently reported a neutron-powder diffraction study of $Nd_{1.845}Ce_{0.155}CuO_{4-\delta}$ and claim oxygen removal by annealing. In this Rapid Communication, we report results from our ongoing studies of oxygen stoichiometry in the cuprate superconductors.

The $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$ samples used in these studies were prepared by firing a powdered mixture of Nd_2O_3, CeO_2, and CuO at temperatures between 950 and 1100 °C with a few intermediate regrindings. Parts of this sample were then annealed either under ambient oxygen pressure or in a sealed evacuated quartz tube with a Zr getter, in both cases followed by slow cooling. The Zr gettering produces a bulk superconducting sample with a T_c at onset of 24 K with shielding and Meissner fractions of 30% and 16% at 5 K, respectively, when demagnetizing effects were taken into account. Preliminary x-ray diffraction measurements at 298 K gave virtually identical diffraction patterns which yielded refined values of 3.948(1) and 12.076(3) for the lattice parameters a and c, respectively. Electron-diffraction experiments were performed using a Phillips CM30 transmission electron microscope operated at 300 kV. Diffraction patterns of the [001] and [100] zone axes for both samples show systematic extinctions consistent with the body-centered tetragonal space group $I4/mmm$. Contrary to results for samples studied by Izumi *et al.*[7] no superlattice reflections were visible.

Neutron-powder-diffraction data for the two samples were collected at 11 and 300 K on the high-resolution ($\Delta d/d \approx 1 \times 10^{-3}$) neutron-powder diffractometer (NPD) at the Manuel Lujar, Jr. Neutron Scattering Center (LANSCE) at Los Alamos. For each sample, data were collected in four banks of detectors (at $2\theta = \pm 148°$ and $\pm 90°$) for ≈ 12 h at average proton currents of 38 μA at 15 Hz. Part of the medium d-spacing data taken on the $+148°$ detector bank is shown in Fig. 1. The absence of any unassigned peaks indicates that any secondary phases cannot be present at levels above a percent or so in either sample. It also indicates that the space group assignment is correct and that any lowering of the symmetry (for example by ordering of the cations on the Nd/Ce sites) does not take place, as will be seen later.

The structural models for $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$ were refined using the Rietveld refinement code GSAS.[8] Unlike $La_2CuO_{4+\delta}$, which phase separates into nonsuperconducting La_2CuO_4 and superconducting oxygen-rich phases below about 320 K,[9] it was immediately evident from the data that the crystal symmetry remained the same for
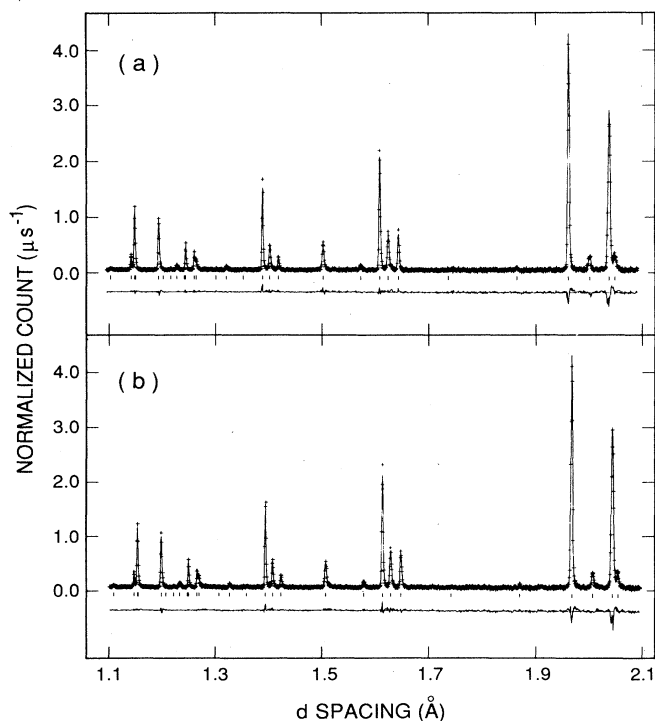
FIG. 1. Part of the neutron diffraction data at 11 K for (a) $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$ after annealing in oxygen and (b) after annealing in an evacuated sealed quartz tube in the presence of a Zr getter. Data shown by plus (+) marks represent only data collected on the +148-degree detector bank of NPD. The continuous line through both sets of data is the calculated profile from the Rietveld refinement that gave the structural parameters listed in Table I. Tick marks below the data indicate the positions for the allowed reflections. The lower curve in each panel represents the difference between the observed and calculated profiles.

both samples at both temperatures. Thus for all four structures, we refined the lattice constants, atomic positions, anisotropic thermal parameters, and oxygen site occupancies with the space group $I4/mmm$. In addition, we refined the usual background, scale factors, diffractometer constants (with the usual exception of the diffractometer C constant which depends primarily on instrument geometry) and profile coefficients (primarily anisotropic strain and particle size). In all refinements, both the atomic coordinate z and the anisotropic thermal parameters for Nd and Ce, which are assumed to occupy the same site with the relative occupancy ratio of 1.85:0.15, are constrained to be the same. The resulting structural parameters (lattice constants a and c, cell volume V, atomic positions z, fractional site occupancy f, anisotropic thermal parameters U_{ii}, and the overall oxygen stoichiometry $4-\delta$) and the weighted profile and expected agreement factors, R_{wp} and R_{exp}, respectively, are given in Table I; the quality of the fit obtained is readily apparent from an examination of the difference curves in Fig. 1. An examination of the parameters in Table I shows that the structure changes very slightly with temperature: For both samples, a increases 0.19% and c increases 0.24%, to

give an overall volume expansion of 0.62%. These observed thermal expansion coefficients are quite similar to those observed by us for $La_{2-x}Sr_xCuO_4$.[10] The structure also changes very little with Zr gettering, with the lattice parameter a increasing slightly and c decreasing slightly. The only variable atomic coordinate (z for Nd/Ce) remains identical within the estimated standard deviations at the two corresponding temperatures. With the exception of U_{33} for Nd/Ce, all anisotropic thermal parameters also remain identical. The only difference that appears larger than one standard deviation is U_{33} for Nd/Ce, which increases substantially (more than 3σ) with annealing at both temperatures, but especially so at 11 K. This elongation of the thermal parameter along the z axis at both temperatures suggests a very slight increase in the static displacements of the Nd/Ce atoms. However, it is not clear whether or not this difference is really significant; and if it is significant, what it implies about the transition to bulk superconductivity. The thermal parameters for the oxygen atoms are comparable in magnitude to those found for $La_{2-x}Sr_xCuO_4$:[10] O(1), which forms two-dimensional sheets with the Cu ions again exhibits oblate thermal ellipsoids which indicate larger amplitudes of motion transverse to the O(1)−Cu−O(1) bonds; O(2), which together with the O(1) ions form a cubic array about the Nd/Ce ions, exhibit nearly spherical thermal ellipsoids at low temperatures that elongate along the z axis at higher temperatures. The fractional occupancy at the O(2) site is slightly lower than that for O(1), but there is essentially no change in occupancy within experimental uncertainty for either of these sites on annealing with a Zr getter. Refinement of the structures for the same samples at the two temperatures provides independent determinations of the oxygen stoichiometry and thus provides an estimate of the accuracy of the refined values for the site occupancy. The differences vary from 0.002 to 0.008 and suggest an accuracy somewhat poorer than the precision of the individual site occupancy refinements which range from ±0.002 to ±0.003. Table II shows the relevant cation-oxygen bond lengths derived from the structures; although all bond lengths increase a little with temperature as would be expected, the bond lengths for the different samples remain remarkably similar at the different temperatures.

An attempt was made to refine the structure in a lower symmetry space group ($P4/nmm$) to allow for partial Nd/Ce ordering. For both samples, this led to poor refinements that were unstable in both occupancies and thermal parameters, indicating that the Nd/Ce cations must remain essentially disordered.

In order to examine the possibility of oxygen insertion and/or depletion in sites other than the ones considered, we compared Fourier plots of the observed data and Fourier difference plots of atomic densities (between the observed data and the prediction from the refined structures) along the [100] and [110] planes for both samples. The $only$ difference contours which appeared in the as-prepared sample that were absent in the Zr-gettered sample appeared at an approximate atomic position of (0,0,0.204). This corresponds to the apical oxygen sites of the elongated CuO_6 octahedra in the T-phase compounds,

TABLE I. Structural parameters for $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$ oxygenated and following Zr gettering at 11 and 300 K. Space group $I4/mmm$: $Cu(0,0,0)$, $Nd/Ce(0,0,z)$, $O(1)(0,\frac{1}{2},0)$, and $O(2)(0,\frac{1}{2},\frac{1}{4})$. Lattice constants are given in units of Å, cell volumes in $Å^3$, thermal parameters in $Å^2$ and agreement factors in percent. The numbers in parentheses following refined parameters represent the estimated standard deviations in the last significant digit(s).

	Parameter	Oxygenated		Zr gettered	
		11 K	300 K	11 K	300 K
	a	3.94097(5)	3.94844(6)	3.94160(4)	3.94908(6)
	c	12.05997(15)	12.08862(19)	12.05922(15)	12.08802(18)
	V	187.307(7)	188.464(8)	187.354(6)	188.515(8)
Cu	U_{11}	0.00269(7)	0.00576(10)	0.00280(7)	0.00583(9)
	U_{33}	0.00439(14)	0.00972(21)	0.00411(14)	0.00965(20)
Nd/Ce	z	0.35252(2)	0.35232(3)	0.35255(2)	0.35231(2)
	U_{11}	0.00154(5)	0.00506(8)	0.00163(5)	0.00526(7)
	U_{33}	0.00184(8)	0.00528(12)	0.00215(9)	0.00568(13)
O(1)	f	0.990(2)	0.992(3)	0.986(2)	0.993(3)
	U_{11}	0.00582(14)	0.01126(20)	0.00566(14)	0.01160(20)
	U_{22}	0.00385(13)	0.00666(18)	0.00365(12)	0.00681(17)
	U_{33}	0.00698(15)	0.01299(21)	0.00696(15)	0.01311(21)
O(2)	f	0.983(2)	0.975(3)	0.979(2)	0.977(3)
	U_{11}	0.00447(8)	0.00689(11)	0.00457(8)	0.00698(11)
	U_{33}	0.00500(14)	0.00945(19)	0.00484(14)	0.00948(18)
	$4-\delta$	3.962	3.946	3.946	3.950
	R_{wp}	5.92	5.86	5.81	5.53
	R_{exp}	4.09	4.08	4.03	3.84

and presents a plausible site for excess oxygens in the T' phase compounds. We attempted refinement of the oxygen occupancy at these positions: First refining the atomic positions and occupancy with fixed estimated values of an isotropic thermal parameter for the oxygenated sample, and then refining the occupancies of the Zr-gettered sample with both atomic position and thermal parameter fixed. The resulting occupancies at 11 and 300 K are 0.008(2) and 0.006(2), respectively, for the oxygenated sample and 0.008(2) and 0.005(2) for the Zr-gettered sample. The resulting occupancies are essentially zero within the accuracy of the refinement and the small differences cannot be responsible for any differences in oxygen stoichiometry in the two samples.

The difficulty in locating oxygen excess or deficiency in

TABLE II. Selected cation-oxygen bond lengths for $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$ oxygenated and following Zr gettering at 11 and 300 K. The numbers in parentheses following refined parameters represent the estimated standard deviations in the last significant digit(s) resulting from the refinement.

	Oxygenated		Zr gettered	
	11 K	300 K	11 K	300 K
Nd/Ce-O(1)	2.6545(2)	2.6617(2)	2.6544(2)	2.6620(2)
Nd/Ce-O(2)	2.3263(1)	2.3297(2)	2.3267(1)	2.3299(2)
Cu-O(1)	1.9705(1)	1.9742(1)	1.9708(1)	1.9745(1)

the 2:1:4 cuprates is illustrated in recent work on superconducting $La_2CuO_{4+\delta}$ by Jorgensen *et al.*[9] and Chaillout *et al.*[11] Using neutron-powder diffraction, Jorgensen *et al.*[9] showed that below 320 K $La_2CuO_{4+\delta}$, annealed in a high pressure of O_2, consists of two nearly identical orthorhombic phases, one of which is similar to the stoichiometric sample with $\delta = 0$ and another which is oxygen rich and is presumably the superconducting phase. However, the presence of both phases and the similarity in their structures made it impossible to uniquely locate the excess oxygen atoms within the latter phase. Chaillout *et al.*[11] refined structures from single-crystal neutron diffraction at room temperature and were able to find that the excess oxygen atoms enter sites analogous to the O(2) sites in $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$; however, the apical oxygens on the elongated CuO_6 tetrahedra must be displaced substantially to accommodate this site occupancy. In a recent study of $La_2NiO_{4+\delta}$, Jorgensen *et al.*[12] found that the excess oxygen occupied the T' phase O(2) sites. Since the excess oxygens in the T phase compounds occupy the approximate O(2) sites of the T' phase, the most likely choice for excess oxygens in the T' phase compounds are the vacant apical sites of the T phase. The results of our refinements for both oxygenated and Zr-gettered $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$ show that the occupancies for the apical sites are essentially zero to within the estimated accuracy of Rietveld refinement for site occupancy.

Tokura *et al.*[1] used iodometric titration, assuming the reduction of Ce^{4+} to Ce^{3+}, to estimate an increase of

≈ 0.07 in the number of oxygen vacancies on annealing. However, the use of iodometric titration to determine oxygen content assumes a knowledge of which cations or anions are being reduced and then assumes charge balance to determine oxygen content.[7] Thus the validity of this result depends on a knowledge of the oxidation states of Ce; although Izumi et al.[13] have claimed that it is $+4$ in the T^* phase compound $Nd_{1.32}Ce_{0.27}Sr_{0.41}CuO_{4-\delta}$ on the basis of the similarity of x-ray photoemission data with that for CeO_2, it is generally thought that the Ce oxidation state in CeO_2 is actually closer to $+3.5$.[14,15] If one takes this into account, then the implied oxygen vacancy should be twice as large as that estimated by Tokura et al.[1] Furthermore, the observed filling of the $3d$ holes on the Cu ions with Ce doping[5] would further complicate interpretation of the titration results because the presence of Cu^+ ions would alter the charge balance without affecting the titration; this would lead to an overestimate of the oxygen stoichiometry. These two unknown partially offsetting corrections make it impossible to determine oxygen stoichiometry using a simple iodometric titration. Moran et al.[6] using both a modified iodometric titration technique (sensitive to Cu^+ as well and estimated to be accurate to < 0.03)[16] and thermogravimetric analysis estimate that the oxygen stoichiometry decreases from 4.05 to 4.03 in $Nd_{2-x}Ce_xCuO_{4-\delta}$ as x decreases from 0.15 to 0. Their resultant overall stoichiometry of > 4.0 is surprising but their samples were contaminated with several oxide impurities which may complicate their interpretation. Thermogravimetric analysis of our samples in both reducing and oxidizing atmospheres showed that the oxygenated and Zr-gettered samples did not differ in oxygen content by more than 0.02 in the formula and confirm results from our neutron site-occupancy refinements.

Interestingly, in the only other neutron scattering study of the structure to date, Izumi et al.[8] make a claim for oxygen depletion on annealing that is not supported by their structural refinement. The results from their refinement shows that the overall oxygen stoichiometry decreases from 3.926(24) to 3.922(46) when their samples are annealed in a low-O_2 partial pressure; these values lie well within their estimated errors and are essentially identical. Moreover, their analysis for oxygen stoichiometry is incomplete in that they only refined the occupancies of the two oxygen sites in the Nd_2CuO_4 structure; they did not investigate the possibility of oxygen occupancy of the apical T-phase sites or of other possible defect sites.

The virtual absence of any structural changes or changes in oxygen content raises the question as to what changes are induced by the Zr-gettering process that transforms the nonsuperconducting oxygenated material into a bulk superconductor. It has already been shown that the Nd/Ce cation ordering does not take place and that they remain disordered for both as-prepared and Zr-gettered samples. Another explanation could be valence ordering between Ce ions and the Cu ions or among the Cu ions themselves. However, since the structure and composition do not change with annealing, it is difficult to understand why annealing would be necessary for any postulated valence ordering.

[1]Y. Tokura, H. Takagi, and S. Uchida, Nature (London) **337**, 345 (1989).

[2]Hk. Müller-Buschbaum and W. Wollschläger, Z. Anorg. Allg. Chem. **414**, 76 (1975).

[3]H. Takagi, S. Uchida, and Y. Tokura, Phys. Rev. Lett. **62**, 1197 (1989).

[4]S. Uchida et al., Jpn. J. Appl. Phys. **26**, L440 (1987).

[5]J. M. Tranquada et al., Nature (London) **337**, 720 (1989).

[6]E. Moran et al., Physica C (to be published).

[7]F. Izumi et al., Physica C **158**, 433 (1989).

[8]A. C. Larson and R. B. Von Dreele, Los Alamos National Laboratory Report No. LA-UR-86-748, 1987 (unpublished).

[9]J. D. Jorgensen et al., Phys. Rev. B **38**, 11 337 (1988).

[10]G. H. Kwei, A. Williams, and A. C. Larson (unpublished).

[11]C. Chaillout et al., Physica C **158**, 183 (1989).

[12]J. D. Jorgensen et al., Phys. Rev. B **40**, 2187 (1989).

[13]F. Izumi et al., Physica C **158**, 440 (1989).

[14]D. D. Koelling, A. M. Boring, and J. H. Wood, Solid State Commun. **47**, 227 (1983).

[15]A. Kotani, H. Mizuta, T. Jo, and J. C. Parlebas, Solid State Commun. **53**, 805 (1985); T. Jo and A. Kotani, ibid. **54**, 451 (1985).

[16]A. I. Nazzal et al., Physica C **153-155**, 1367 (1988).