Structural Transition in the La$_{2-x}$Nd$_x$CuO$_4$ System

Alvaro W. Mombrú[1]

Laboratorio de Cristalografía, Cátedra de Física, Facultad de Química, CC 1157, CP 11800, Montevideo, Uruguay

and

Alexandros Lappas and Kosmas Prassides

School of Chemistry and Molecular Sciences, University of Sussex, Brighton BN1 9QJ, United Kingdom

The structural transition in the La$_{2-x}$Nd$_x$CuO$_4$ system is studied through the $x = 0.45$, 0.5 compositions, using neutron powder diffraction. Both compositions could be refined as biphasic systems represented by the *I4/mmm* and the *Abma* space groups. The presence of T and T′ phases could be observed in both compositions. The apical oxygen atom in the copper coordination octahedron can be regarded as the key for structural distortion causing the transition from T to T′ structures. © 1998 Academic Press

INTRODUCTION

The presence of layers of corner-sharing square CuO$_4$ units is a common structural feature of the superconducting copper oxide ceramics (1). Crucial to the understanding of the transition from superconducting to insulating behavior is the study of the structural evolution of the copper–oxygen sheets as a function of temperature and composition. In particular, the rare earth copper oxides of stoichiometry RE_2CuO$_{4+\delta}$ (RE = rare earth) present three structure types called T, T′, or T* structure depending on the copper ion environment. The T structure is characterized by an octahedral environment of oxide ions surrounding Cu^{2+}. The largest rare earth ion cuprate, La$_2$CuO$_{4+\delta}$, crystallizes in a slightly distorted K$_2$NiF$_4$ T structure (2). In the T′ structure the copper ion is coordinated to a square of oxide ions, as occurs in Nd$_2$CuO$_4$. The T* structure presents a square pyramid as the coordination polyhedron around the copper ion.

La$_2$CuO$_{4+\delta}$ crystal structure appears to be very simple, with the (CuO$_2$)$^{2-}$ layers being part of the strongly elongated CuO$_6$ octahedra (3, 4), separated by rock-salt-like La–O layers. La$_2$CuO$_{4+\delta}$ is extremely sensitive to changes

in oxygen stoichiometry (5), ranging from an antiferromagnetic semiconductor with a Néel temperature of 257 K (6) to a metal and even becoming a high T_c superconductor when doped with holes by partially replacing lanthanum with alkaline-earth ions or adding excess oxygen into the structure (7).

Changing the lanthanide ion from La^{3+} to Pr^{3+} or Nd^{3+} leads to the related T′ structure (8). This is due to the intermediate size of the rare earth ion in the range (Pr–Gd). In contrast to La$_2$CuO$_{4+\delta}$, neodymium cuprate exhibits superconductivity when electron-doped by introducing Ce^{4+} in the network, replacing the neodymium ion (9–15). In the cuprate Nd$_{1.85}$Ce$_{0.15}$CuO$_4$, oxygen content is crucial to the superconducting properties, as in the lanthanum cuprate.

The relative simplicity of these rare earth systems allows us to examine how structure is related to ionic size effects and cation ordering. The study of the solid solubility of La$_2$CuO$_4$ (T) and Nd$_2$CuO$_{4+\delta}$ (T′) provides a measure of the relative stabilities of these structural types.

It is well known that in the La$_{2-x}$Nd$_x$CuO$_4$ system, the phases with $x < 0.5$ exhibit the T structure and the phases with $x > 0.6$ exhibit the T′ structure.

Some authors (6, 16) have studied the T–T′ transition and explained it in terms of an ionic model, in which there is competition between lanthanide and copper ions for bonding with the apical oxide in La$_2$CuO$_4$. In the T′ phase the Cu–O bond length elongates with respect to the equatorial Cu–O one in the T phase, and the Nd–O bond distances are shorter than La–O ones. This evidence suggests that the RE–O layer is the primary driving force in this T–T′ transition.

The purpose of this study is to determine the structure of two almost symmetrical compositions in the transition region, La$_{1.55}$Nd$_{0.45}$CuO$_4$ and La$_{1.5}$Nd$_{0.5}$CuO$_4$, by means of careful Rietveld analysis of high-resolution neutron data.

[1] Author to whom correspondence should be addressed.

EXPERIMENTAL AND RESULTS

(a) Samples Preparation

The $x = 0.45$ and 0.5 samples of the $La_{2-x}Nd_xCuO_4$ system used in the experiment were prepared by solid state reaction. Stoichiometric amounts of CuO, La_2O_3, and Nd_2O_3 were thoroughly mixed and fired at $1000°C$ in air for 24 h. The powder was ground, and the process was repeated three times. The reaction development was followed by powder X-ray diffraction using a D-5000 Siemens diffractometer. Extra annealing treatments of 24 h were performed to ensure that the reaction was completed and that homogeneous samples were obtained.

(b) Experimental Procedure

These samples were measured using neutrons of wavelength 1.594 Å. The measurements were performed using D2B, at the Institute Laue Langevin (ILL), Grenoble, at $T = 4.98$ K between $2\theta = 10.00°$ and $2\theta = 149.95°$ in steps of $0.05°$.

The refinements were carried out with the Rietveld method (17) program PROFIL (18) for multiphasic samples, incorporating a pseudo-Voigt function peak shape description. The background data used in these refinements were read from a file with previously estimated values (56 and 80 background points for $x = 0.45$ and 0.50, respectively).

The first refinements based on neutron powder intensity data were made assuming monophasic samples. In the orthorhombic *Abma* space group, the unit cell involves a $\sqrt{2} \times \sqrt{2}$ expansion of the basal plane of the tetragonal $I4/mmm$ unit cell. No acceptable results were obtained separately for the $I4/mmm$ or for the *Abma* space group, due to the evidence of many unindexed peaks. In both samples the Rietveld analysis performed using any of these models gave very poor results with typical R parameters greater than 20%.

However, it was possible to index all peaks as belonging to either of those space groups. This unambiguosly implies the existence of a biphasic system with the presence of the $I4/mmm$ and *Abma* space groups as shown in Fig. 1.

The present work shows Rietveld analysis of biphasic systems with $I4/mmm$ and *Abma* space groups for both compositions $La_{2-x}Nd_xCuO_4$ ($x = 0.45$, 0.5) (34 refined parameters).

The crystal structure data for the $x = 0.45$ and 0.5 compositions are shown in Tables 1 and 2 and the main bond distances and angles in Table 3. Observed, calculated, and
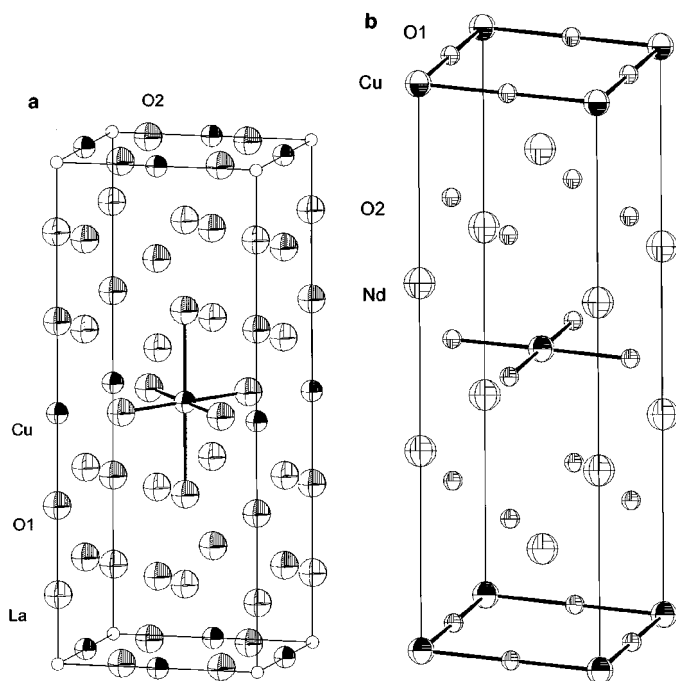

FIG. 1. Crystal structures of La_2CuO_4. *Abma* space group (a), and Nd_2CuO_4, $I4/mmm$ space group (b).

TABLE 1
Final Structural Parameters from the Rietveld Refinements of $La_{1.55}Nd_{0.45}CuO_4$ at $T = 4.98$ K

Space group	$I4/mmm$	*Abma*
Percentage by weight	8.8	91.2
$a/\text{Å}$	3.9867(2)	5.3923(2)
$b/\text{Å}$		5.3393(1)
$c/\text{Å}$	12.447(2)	13.0326(4)
$V/\text{Å}^3$	197.84(3)	375.227(3)
$x(Cu)$	0	0
y	0	0.5
z	0	0
$B/\text{Å}^2$	0.74(2)	0.25(3)
Occupancy	2.0	4.0
$x(O(1))$	0	$-0.0037(2)$
y	0.5	0.5
z	0	0.1834(2)
$B/\text{Å}^2$	1.6(5)	1.18(6)
Occupancy	3.8(3)	8.04(6)
$x(O(2))$	0.5	0.25
y	0	0.25
z	0.25	0.0093(3)
$B/\text{Å}^2$	1.0(5)	1.0(5)
Occupancy	3.7(3)	7.99(5)
$x(Nd/La)$	0	0.0084(2)
y	0	0.5
z	0.3521(4)	0.36186(6)
$B/\text{Å}^2$	0.64(1)	0.26(1)
Occupancy	2(1)/2(1)	1.6(2)/6.4(2)
$RI/\%$	10.99	5.13
$R_e/\%$	4.21	1.99
$R_{wp}/\% \ (R_e/\%)$	12.40(2.84)	
$R_{tot}/\% \ (R_{tot,exp}/\%)$	8.55(1.91)	

TABLE 2
Final Structural Parameters from the Rietveld Refinements of La$_{1.5}$Nd$_{0.5}$CuO$_4$ at $T = 4.98$ K

Space group	$I4/mmm$	$Abma$
Percentage by weight	93.6	6.4
a/Å	3.98591(2)	5.398(2)
b/Å		5.328(2)
c/Å	12.4440(3)	13.064(4)
V/Å^3	197.703(4)	375.8(2)
x(Cu)	0	0
y	0	0.5
z	0	0
B/Å^2	0.49(3)	0.4011(8)
Occupancy	2.0	4.0
x(O(1))	0	0.03(2)
y	0.5	0.5
z	0	0.178(3)
B/Å^2	0.58(5)	1.2(7)
Occupancy	4.01(4)	8.14(6)
x(O(2))	0.5	0.25
y	0	0.25
z	0.25	0.000(3)
B/Å^2	0.60(5)	0.5(5)
Occupancy	3.99(4)	8.0(4)
x(Nd/La)	0	$-0.021(3)$
y	0	0.5
z	0.35159(5)	0.3625(8)
B/Å^2	0.40(1)	0.6(2)
Occupancy	1.05(5)/2.95(5)	1(1)/7(1)
RI/%	3.18	8.87
R_e/%	2.09	6.83
R_{wp}/% (R_e/%)	11.86(2.42)	
R_{tot}/% ($R_{tot,exp}$/%)	8.06(1.66)	

TABLE 3
Selected Bond Distances (Å) and Angles (deg) in La$_{1.55}$Nd$_{0.45}$CuO$_4$ and La$_{1.5}$Nd$_{0.5}$CuO$_4$ at $T = 4.98$ K

	La$_{1.55}$Nd$_{0.45}$CuO$_4$	La$_{1.5}$Nd$_{0.5}$CuO$_4$
Phase 1, $I4/mmm$		
Cu–O(1)	1.9934(1)	1.9930(1)
La/Nd–O(1)	2.713(3)	2.7171(4)
La/Nd–O(2)	2.364(3)	2.3601(3)
O(1)–Cu–O(1)	90	90
Phase 2, $Abma$		
Cu–O(1)	2.399(3)	2.33(4)
Cu–O(2)	1.9010(2)	1.8962(1)
La/Nd–O(1)	2.339(3)	2.42(4)
La/Nd–O(1)	2.518(3)	2.50(7)
La/Nd–O(1)	2.7386(7)	2.717(8)
La/Nd–O(2)	2.558(3)	2.55(3)
La/Nd–O(2)	2.678(3)	2.67(3)
O(1)–Cu–O(1)	90	90
O(1)–Cu–O(2)	89.8(1)	87(1)
O(2)–Cu–O(2)	89.2(1)	89.26(1)

A comparison between the lattice parameters in both compositions shows that the c axis contracts 5% in the transition from T to T′ structure. In contrast, the basal plane and the unit cell volume increase in the same transition (5% for x and y axis; 5% for volume) as shown in a previous report (6).

Although there is an increase in the Cu–O bond lengths for the T and T′ phase from the $x = 0.5$ and 0.45 composition, this increase is meaningless in the T′ phase, from 1.9930(1) to 1.9934(1) Å and totally due to the changes in the cell parameters. In the T phase the main increase is in
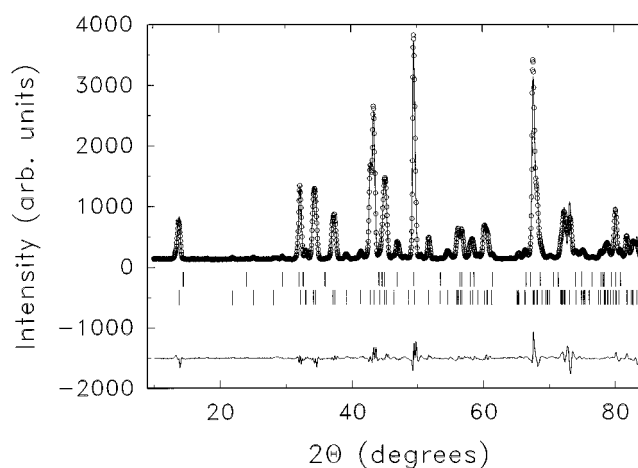
difference profiles for $x = 0.45$ are shown in Figs. 2 and 3. The profiles for $x = 0.5$ are shown in Figs. 4 and 5.

DISCUSSION

It is possible to deduce by inspection of the data pattern the lower symmetry of the crystal structure for the $x = 0.45$ than the $x = 0.5$ composition. The Rietveld refinements led to biphasic systems where the percentage by weight of T and T′ structures are 91.2% and 8.8% for $x = 0.45$ and 6.4% and 93.6% for $x = 0.5$. Suitable constraints were included to refine the occupancies of Nd and La, to preserve global stoichiometry of the compositions. The refined compositions for both structures (T and T′) are La$_{1.6}$Nd$_{0.4}$CuO$_{4.0}$ and LaNdCuO$_{3.8}$ for $x = 0.45$ and La$_{1.7}$Nd$_{0.3}$CuO$_{4.0}$ and La$_{1.47}$Nd$_{0.53}$CuO$_{4.0}$ for $x = 0.5$. The La and Nd concentrations for the minor phase in each composition (T′ for $x = 0.45$ and T for $x = 0.5$) are not as accurate as those for the corresponding major phases, as can be inferred from the uncertainty in the refined occupancies (see Tables 1 and 2).

FIG. 2. Neutron diffraction profile (hollow circles) of La$_{1.55}$Nd$_{0.45}$CuO$_4$ and Rietveld refinement (full line). Upper tick marks show the positions for the $I4/mmm$ space group, and lower tick marks show the positions for the $Abma$ space group; 2θ range 15–85°.
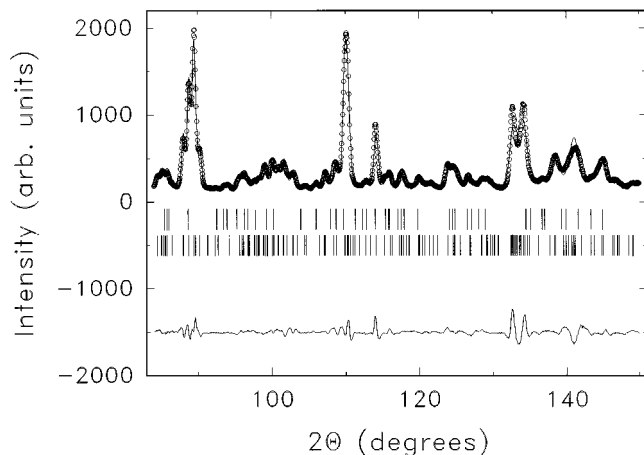
FIG. 3. Neutron diffraction profile (hollow circles) of $La_{1.55}Nd_{0.45}CuO_4$ and Rietveld refinement (full line). Upper tick marks show the positions for the $I4/mmm$ space group, and lower tick marks show the positions for the $Abma$ space group; 2θ range 85–150°.

FIG. 5. Neutron diffraction profile (hollow circles) of $La_{1.5}Nd_{0.5}CuO_4$ and Rietveld refinement (full line). Upper tick marks show the positions for the $I4/mmm$ space group, and lower tick marks show the positions for the $Abma$ space group; 2θ range 85–150°.

the copper–apical oxygen bond (Cu–O(1)), from 2.33(4) to 2.399(3) Å, while the copper–equatorial oxygen (Cu–O(2)) bond length elongates, from 1.8962(1) to 1.9010(2) Å. For the T phase these differences cannot be explained on the basis only of changes in the cell parameters. It can be observed that the copper coordination octahedron is distorted from $x = 0.45$ to 0.5 composition (when the average rare earth ion size decreases), as can be deduced from the O(1)–Cu–O(2) angle, which changes from 89.8(1) to 87(1)°.

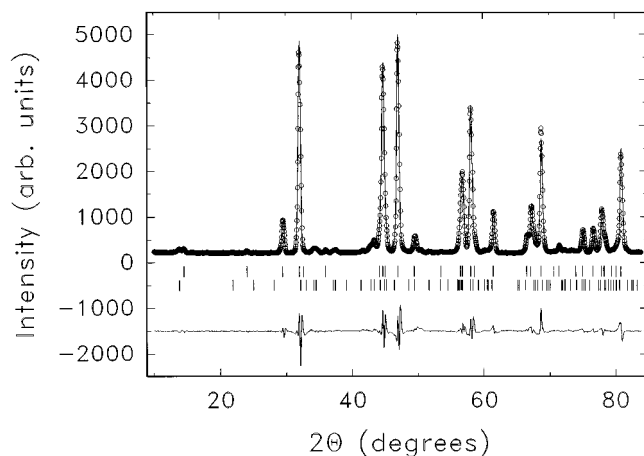The average rare earth ion size is 1.134 and 1.1325 Å for the $x = 0.45$ and 0.5 compositions, respectively.

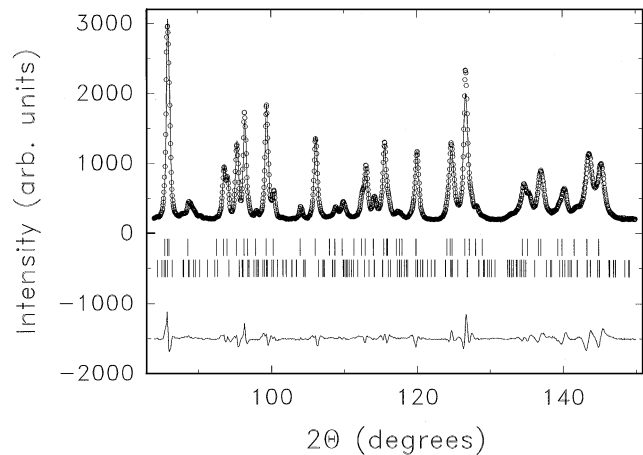**FIG. 4.** Neutron diffraction profile (hollow circles) of $La_{1.5}Nd_{0.5}CuO_4$ and Rietveld refinement (full line). Upper tick marks show the positions for the $I4/mmm$ space group, and lower tick marks show the positions for the $Abma$ space group. 2θ range 15–85°.

When this rare earth ion size increases, RE–O(1) shortens from 2.7171(4) to 2.713(3) Å and RE–O(2) is enlarged from 2.3601(3) to 2.364(3) Å, for the T′ phase. These changes are not important and are determined not only by the cell parameter expansion but by the refinement of the z coordinate in the RE^{3+} ion as well.

The RE–O distances in the T phase exhibit important changes from $x = 0.5$ to 0.45 compositions (average rare earth ion size 1.1325 to 1.134 Å, respectively). The most important change is the shortening of one of the RE–O(1) bonds, from 2.42(4) to 2.339(3) Å. This is the bond that connects the apical oxygen atom in the octahedron surrounding the copper ion with the RE^{3+} ion with coordinates ($\cong 0, \frac{1}{2}, z$). The other RE–O(1) bond distances enlarge from 2.50(7) to 2.518(3) Å and from 2.717(8) to 2.7386(7) Å. The RE–O(2) bond distances increase insignificantly, from 2.55(3) to 2.558(3) Å and from 2.67(3) to 2.678(3) Å.

When traversing from T to T′ the main feature is the distortion of the copper coordination octahedron and the modification of all bonds related to the apical oxygen atom O(1), especially the ones that are directed mainly along the c axis. These RE–O(1) and Cu–O(1) bonds exhibit structural tension and compression, indicating a decrease in structural stability. This transition can therefore be regarded as a structural modification due to the connection of RE^{3+} and Cu^{2+} ions with the apical oxygen atom in the copper coordination octahedron, as predicted by the ionic model formerly depicted (6). The key for the structural transition is this O(1) atom, and by regulating the structural coordinates of the atoms connecting to it, it is possible to increase the distortion of the copper coordination octahedron and perform the T–T′ transition for RE_2CuO_4 cuprates as a way to accommodate the smaller size rare earth ion.

In summary, the T–T′ transition can be viewed as the coexistence of a T structure (richer in La) and a T′ (richer in Nd), where stabilization is ruled by structural tension and compression that is shown in the Cu coordination polyhedra and the *RE*–O bonds.

ACKNOWLEDGMENTS

REFERENCES

1. J. G. Bednorz and K. A. Müller, *Z. Phys. B* **64,** 189 (1986).
2. C. Chaillout, S. W. Cheong, Z. Fisk, M. S. Lehmann, M. Marezio, B. Morosin, and J. E. Schirber, *Physica C* **158,** 183 (1989).
3. T. Freltoft, G. Shirane, S. Mitsuda, J. P. Remeika, and A. S. Cooper, *Phys. Rev. B* **37,** 137 (1988).
4. M. J. Rosseinsky, K. Prassides, and P. Day, *Physica C* **161,** 21 (1989).
5. P. Day, M. Rosseinsky, K. Prassides, W. I. F. David, O. Moze, and A. Soper, *J. Phys. C: Solid State Phys.* **20,** L429 (1987).
6. J. F. Bringley, S. S. Trail, and B. A. Scott, *J. Solid State Chem.* **86,** 310 (1990).
7. A. Kussmaul, Ph.D. Thesis, Massachusetts Institute of Technology, Department of Physics, Cambridge, MA, 1992.
8. M. K. Crawford, R. L. Harlow, E. M. McCarron, W. E. Farneth, J. D. Axe, H. Chou, and Q. Huang, *Phys. Rev. B* **44,** 7749 (1991).
9. T. Chattopadhyay, P. J. Brown, U. Köbler, and V. L. Sobolev, *Physica C* **177,** 294 (1991).
10. M. J. Rosseinsky, K. Prassides, and P. Day, *J. Chem. Soc., Chem. Commun.* 1734 (1989).
11. M. J. Rosseinsky, K. Prassides, and P. Day, *Inorg. Chem.* **30,** 2680 (1991).
12. M. J. Rosseinsky and K. Prassides, *Physica C* **162–164,** 522 (1989).
13. M. J. Rosseinsky and K. Prassides, *Europhys. Lett.* **14,** 551 (1991).
14. S. Shamoto, T. Kiyokura, M. Sato, K. Kakurai, Y. Nakamura, and S. Uchida, personal communication.
15. B. Keimer, R. J. Birgeneau, A. Cassanho, Y. Endoh, M. Greven, M. A. Kastner, and G. Shirane, *Z. Phys. B* **91,** 373 (1993).
16. C. N. R. Rao and A. K. Ganguli, *Acta Crystallogr., Sect. B* **51,** 604 (1995).
17. H. M. Rietveld, *J. Appl. Crystallogr.* **2,** 65 (1969).
18. J. K. Cockcroft, "PROFIL Program," Version 4.10 (1991).