JOURNAL OF SOLID STATE CHEMISTRY 118, 170–175 (1995)

Structure of $La_5Cu_5O_{13.35}$ by High-Resolution Synchrotron X-Ray Diffraction

S. J. La Placa, J. F. Bringley,[1] and B. A. Scott

IBM Research Division, Thomas J. Watson Research Center, Yorktown Heights, New York 10598

and

D. E. Cox

Department of Physics, Brookhaven National Laboratory, Upton, New York 11973

Received September 12, 1994; in revised form February 7, 1995; accepted February 9, 1994

The structure of $La_5Cu_5O_{13.35}$ was refined from high-resolution synchrotron X-ray diffraction data using the Rietveld method. The unit cell is monoclinic, space group $P2/m$–C^12h (No. 10), with a = 8.62884(5) Å, b = 3.83076(2) Å, c = 8.65148(5) Å, β = 90.2166(4)°, V = 285.973(4) Å^3, Z = 1, D_x = 7.085 g/cm^3 at T = 300 K. 265 independent reflections were included in the refinement and a reasonably good fit was obtained with final R values R_I = 9.28%, R_p = 14.51%, R_{wp} = 19.60%, and goodness-of-fit S_{wp} = 1.573. The structure is of the oxygen-defect Perovskite type and is composed of one distorted CuO_6 octahedron and four distorted CuO_5 square pyramids per crystallographic unit cell. The polyhedra of $La_5Cu_5O_{13+\delta}$ display a three-dimensional connectivity with a unique oxygen ordering which creates one-dimensional channels of vacancies along the b-axis. © 1995 Academic Press, Inc.

INTRODUCTION

$La_5Cu_5O_{13+\delta}$ lies in the middle region of the oxygen-defect perovskite-like series $LaCuO_{3-\delta}$ (1). This series of compounds is related to the well-known high-temperature superconducting cuprates (2) and provides a simple prototypical model system for characterizing the electronic and magnetic properties of the superconducting and related cuprates. Although superconductivity has not been observed in this system, its range of oxygen stoichiometry, $0.0 \leq \delta \leq 0.5$, is the widest yet found in a cuprate, allowing the formal oxidation state of copper to be varied continuously from +II to +III within the basic Perovskite framework. Because of their relationship to the high-temperature, superconducting cuprates, a knowledge of the structures and crystal–chemical properties of the $LaCuO_{3-\delta}$ defect perovskites is of general interest.

Depending upon composition, three distinct oxygen-defect perovskite-like phases are observed in this system, a tetragonal one with a homogeneity range $0 < \delta < 0.17$, a monoclinic phase with a homogeneity range $0.2 < \delta < 0.38$, and an orthorhombic phase existing over the interval $0.41 < \delta < 0.5$, see Fig. 1 of Ref. (1). The structure of the tetragonal phase at $\delta = 0.05$ has been described elsewhere (3); it undergoes a transformation to rhombohedral symmetry at high pressure (4). The orthorhombic phase at $\delta = 0.5$ is isostructural with $CaMnO_{2.5}$ (5) and has also been reported previously (6). $LaCuO_{3-\delta}$ exhibits metallic conductivity in the tetragonal and monoclinic regions, but is insulating for $\delta = 0.5$ (3).

Herein we report the results of a refinement of the structure of the middle member of this perovskite series, $La_5Cu_5O_{13+\delta}$. The structure is closely related to the tetragonal structure of $La_4BaCu_5O_{13+\delta}$ (7).

EXPERIMENTAL

A polycrystalline sample of $La_5Cu_5O_{13+\delta}$ was prepared by heating the tetragonal form of $LaCuO_3$ (1) in an oxygen atmosphere. A platinum crucible containing $LaCuO_{2.95}$ (7.0 g, 0.012 mole) was heated at a rate of 100°C/hr to 525°C, held there for 12 hr, and cooled at the same rate to near room temperature, all under a flow of 99.995% O_2. Compositions were established by thermogravimetric analysis and by iodometric titration (8) with an accuracy in δ of ± 0.02. The two techniques were in excellent agreement with each other, giving the composition $LaCuO_{2.67}$ (or $La_5Cu_5O_{13.35}$). X-ray powder diffraction confirmed the identity of the product with no observable impurities within the detection limit of our laboratory diffractometer.

High-resolution synchrotron X-ray powder diffraction data were collected at beamline X7A at the Brookhaven National Synchrotron Light Source with a channel cut

[1] Present address: Research Laboratories, Eastman Kodak Co., Rochester, NY, 14650-2033.

0022-4596/95 $12.00
Copyright © 1995 by Academic Press, Inc.
All rights of reproduction in any form reserved.

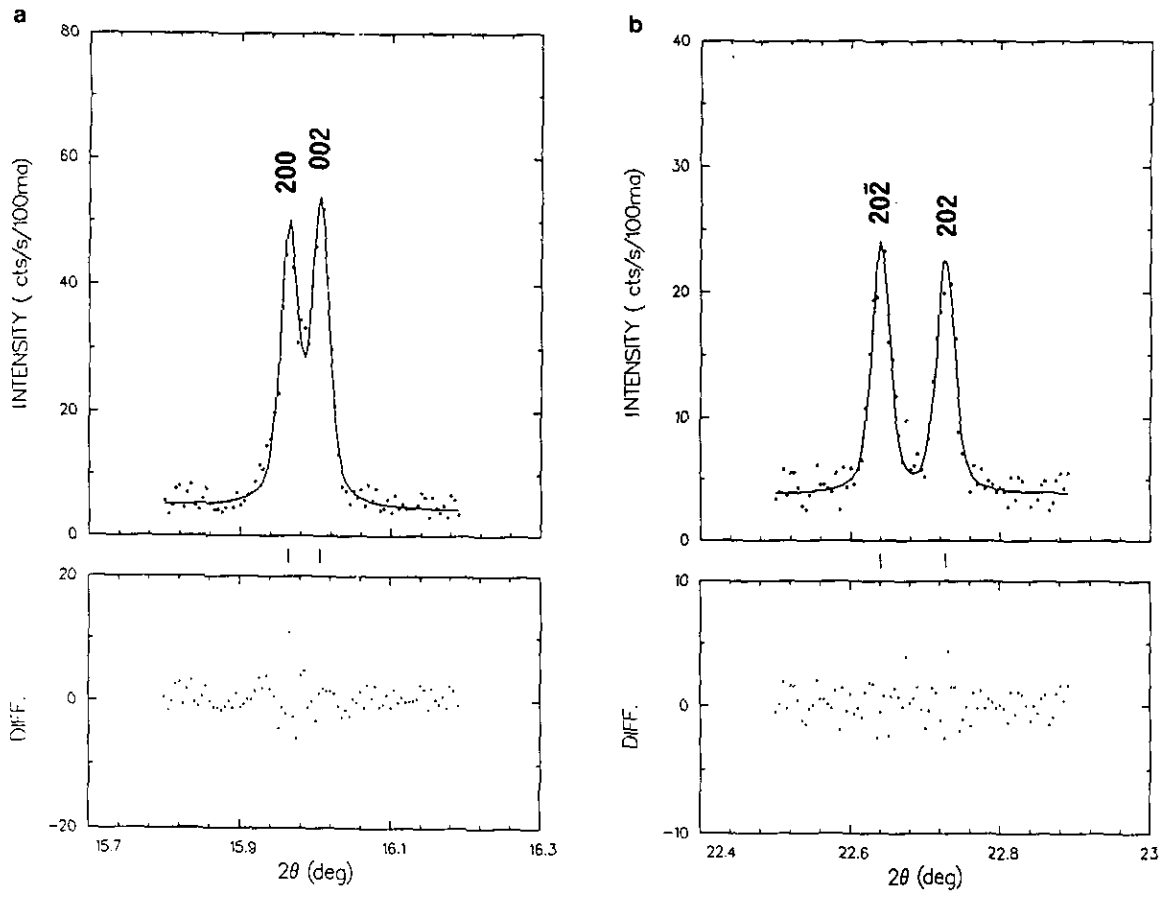

FIG. 1. Diffraction profiles and difference plots showing the monoclinic distortion of $La_5Cu_5O_{13+\delta}$ manifested in the splitting of the pseudo-tetragonal (a) (200) and (b) (220) peaks into monoclinic pairs. The solid line is a least-squares fit to a pseudo-Voigt function.

Si(111) monochromator and a flat Ge(220) analyzer at a wavelength of 1.2015 Å. A sample was packed in a rectangular flat plate holder with a shallow recess, 5 × 1.25 × 0.1 cm in dimension, and step scans were performed at 0.005° intervals over the angular range of 2 θ = 10–64.60° in symmetrical reflection geometry. The samples were rocked 1–2° at each point to obtain a proper powder average over the crystallites. Each measured profile intensity was normalized with respect to the incident beam monitor count measured with an ion chamber and scaled to counts/sec per 100 mA ring current.

STRUCTURAL REFINEMENT

The observed pattern was very well resolved, with peak widths varying from approximately 0.025–0.055° over the range of the data. Several weak peaks characteristic of an $5\frac{1}{2}\ a \times c$ cell analogous to that of $BaLa_4Cu_5O_{13+\delta}$ were evident but split in such a way as to provide unambiguous evidence of a small monoclinic distortion, with a = 8.62884(5) Å, b = 3.83076(2) Å, c = 8.65148(5) Å, and β = 90.22°. This is most readily seen from the splitting of the pseudo-tetragonal (200) and (220) peaks into monoclinic pairs (200, 002) and (202, 20$\bar{2}$), as illustrated in Figs. 1a and 1b. A few weak unidentified impurity peaks were also present at an intensity level of 1–2%. The impurity phase could not be identified from the powder diffraction data file.

Structure refinements were performed using a locally modified version of the Rietveld–Hewat program (9) with a pseudo-Voigt peak-shape function, which approximates the convolution of Gaussian and Lorentzian functions. The atomic scattering factors used were neutral-atom scattering factors for La, Cu, and O from the International Tables for X-ray Crystallography (1974, Vol. IV). A total of 265 independent reflections were included. The parameters refined were the unit cell parameters, five half-width parameters, a zero point correction, an overall scale factor, atomic coordinates, and isotropic temperature factors. Background intensities were estimated by interpolation between values measured in regions well-separated from adjacent peaks, and contributions to each point were calculated over a range of 10 FWHM on each side of a given peak. Impurity peaks were excluded from the

TABLE 1a
Atomic Coordinates and Thermal and Occupancy Parameters of $La_5Cu_5O_{13.35}$ with $P4/m$ Constraints

Atom	Position	x	y	z	B(Å^2)	N
La1	1*h*	0.5	0.5	0.5	2.15(6)	1
La2	2*n*	0.1354(1)	0.5	0.2738(1)	0.64(3)	2
La2′	2*n*	−0.2738	0.5	0.1354	0.64	2
Cu1	1*a*	0.0	0.0	0.0	0.18(9)	1
Cu2	2*m*	0.4249(3)	0.0	0.1719(2)	0.22(5)	2
Cu2′	2*m*	−0.1719	0.0	0.4249	0.22	2
Ox1	1*b*	0.0	0.5	0.0	2.6(6)	1
Ox2	1*d*	0.5	0.0	0.0	2.0	0.07(4)
Ox2′	1*c*	0.0	0.0	0.5	2.0	0
Ox3	2*m*	0.2857(14)	0.0	0.3824(12)	2.4(3)	2
Ox3′	2*m*	−0.3824	0.0	0.2957	2.4	2
Ox4	2*m*	0.2338(12)	0.0	0.0391(10)	−1.5(2)	2
Ox4′	2*m*	0.0391	0.0	0.2338	−1.5	2
Ox5	2*n*	0.4313(14)	0.5	0.1812(13)	2.6(3)	2
Ox5′	2*n*	−0.1812	0.5	0.4313	2.6	2

Note. The B values for O(2) and O(2′) were fixed at 2.0 Å^2 (estimated standard deviations are in parentheses). R_I = 0.0930, R_p = 0.1462, r_{wp} = 0.1968, S_{wp} = 1.578.

TABLE 1b
Atomic Coordinates and Thermal and Occupancy Parameters of $La_5Cu_5O_{13.35}$ with $P2/m$ Symmetry

Atom	Position	x	y	z	B(Å^2)	N
La1	1*h*	0.5	0.5	0.5	2.14(6)	1
La2	2*n*	0.1357(2)	0.5	0.2741(2)	0.62(4)	2
La2′	2*n*	−0.2734(2)	0.5	0.1350(2)	0.67(4)	2
Cu1	1*a*	0.0	0.0	0.0	−0.12(10)	1
Cu2	2*m*	0.4237(4)	0.0	0.1721(4)	0.33(8)	2
Cu2′	2*m*	−0.1717(4)	0.0	0.4260(4)	0.11(8)	2
Ox1	1*b*	0.0	0.5	0.0	2.8(7)	1
Ox2	1*d*	0.5	0.0	0.0	2.0(5)	0.08(4)
Ox2′	1*c*	0.0	0.0	0.5	2.0	0
Ox3	2*m*	0.3020(21)	0.0	0.3854(20)	2.8(5)	2
Ox3′	2*m*	−0.3792(19)	0.0	0.2899(20)	1.7(4)	2
Ox4	2*m*	0.2286(17)	0.0	0.0415(16)	−1.4(3)	2
Ox4′	2*m*	−0.0357(14)	0.0	0.2388(16)	−1.7(3)	2
Ox5	2*n*	0.4309(21)	0.5	0.1797(21)	2.3(5)	2
Ox5′	2*n*	−0.1817(21)	0.5	0.4320(22)	2.6(5)	2

Note. Estimated standard deviations are in parentheses. R_I = 0.0928, R_p = 0.1451, r_{wp} = 0.1960, S_{wp} = 1.573.

refinement. The space group chosen was $P2/m$, which is a subgroup of $P4/m$ assigned to $BaLa_4Cu_5O_{13+\delta}$ (7). Atoms in 4(*j*) and 4(*k*) positions in the latter case divide into two sets of twofold sites for $P2/m$, as can be seen in Tables 1a and 1b. In addition, the 2(*e*) position, which can accommodate excess oxygen, divides into O(2) and O(2′) sites. In the first phase of the refinement, the atom coordinates and temperature factors were refined subject to $P4/m$ constraints, except that an occupancy factor was refined for each of the O(2) and O(2′) sites, with the temperature factor fixed at 2.0 Å^2. However, a slight negative value was found for the latter, and this was fixed at zero in subsequent cycles. A significant improvement was obtained with a preferred orientation correction of the March type (10), with [010] as the preferred axis. The final values are listed at the right-hand side of Table 1a. In the second phase of refinement, the $P4/m$ constraints were gradually released, starting with La(2′), then Cu(2′), followed by the oxygen atoms. The final results are listed at the right-hand side of Table 1b, and the profile fit and difference plot are shown in Fig. 2.

The overall fit is reasoanble, with convergence to the final R values R_I = 9.28%, R_p = 14.51%, R_{wp} = 19.60% and to the goodness-of-fit S_{wp} = 1.573. However, the rather large values for some of the thermal factors indicate the presence of some disorder which has not been properly modeled, which is perhaps the origin of the negative thermal factors observed for O(4) and O(4′). It is somewhat surprising that in spite of the well-defined monoclinic distortion, the atom coordinates hardly deviate from the values obtained with $P4/m$ constraints within the statistical errors. Although the value obtained for the occupancy of the O(2) site appears to be much smaller than that determined by gravimetric analysis, this result is probably not statistically significant, since errors in occupancy factors tend to be underestimated by a factor of 3–4.

It is interesting that Michel *et al.* (7) noted that an oxygen-deficient $BaLa_4Cu_5O_{14-\delta}$ structure would be characterized by monoclinic symmetry, and they did in fact observe that a few crystals exhibited such symmetry in electron diffraction patterns, speculating that this could result from the introduction of oxygen into the tunnels.

DISCUSSION

To date, it has been possible to prepare $La_5Cu_5O_{13+\delta}$ only by reduction of the higher valent $LaCuO_3$. Many attempts were made to prepare $La_5Cu_5O_{13+\delta}$ directly from the binary oxides, La_2O_3 and CuO. Appropriate amounts of the finely divided binary oxides were ground together and heated in pure oxygen at various temperatures ranging from 500 to 800°C. In each case only unreacted starting materials and/or La_2CuO_4 + CuO were observed. Attempts to prepare $La_5Cu_5O_{13+\delta}$ directly by reacting the

FIG. 2. (a, b) Synchrotron X-ray diffraction profiles and difference plots for $La_5Cu_5O_{13.35}$ over the full range of data collected.

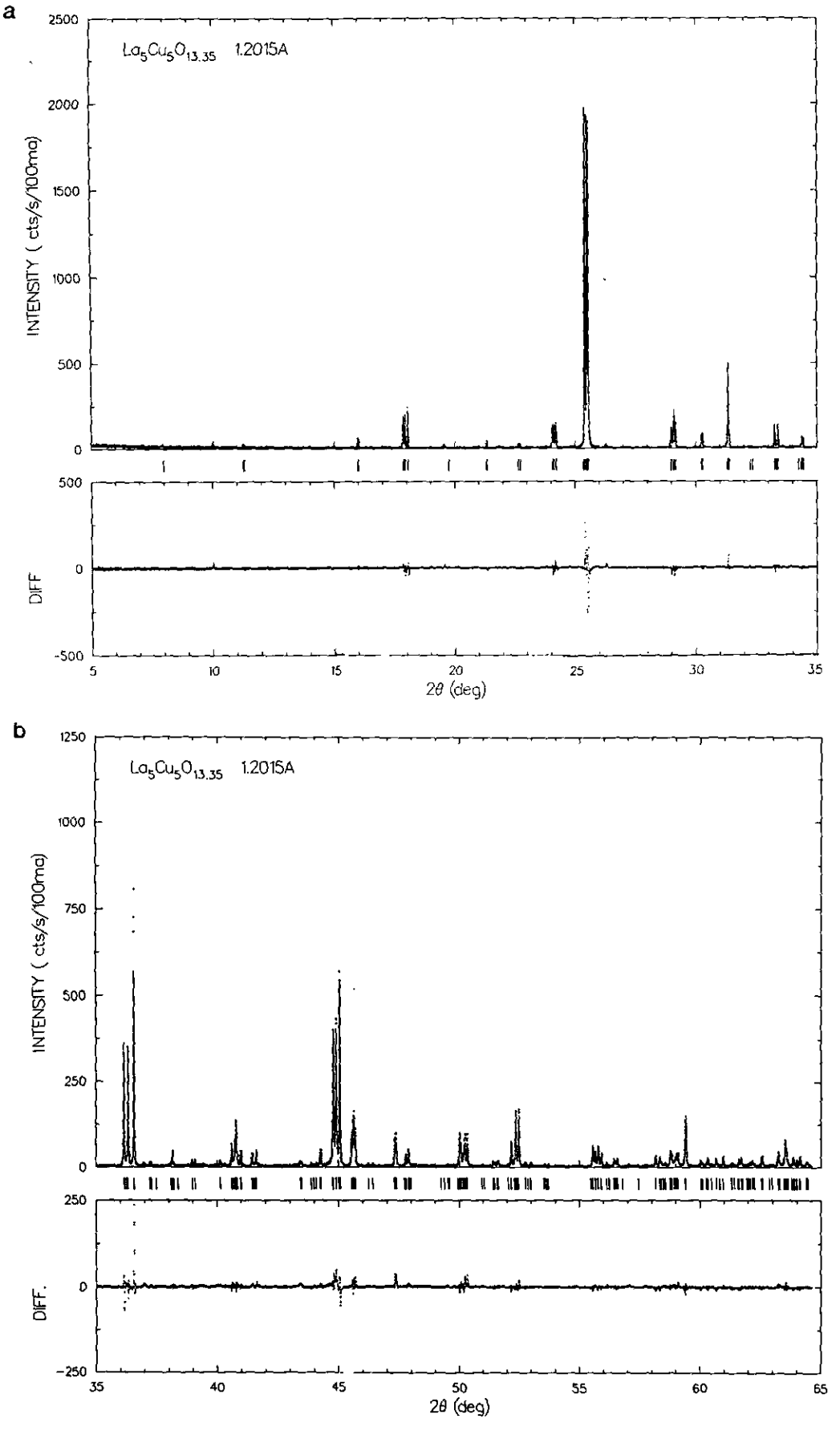
a
$La_5Cu_5O_{13.35}$ 1.2015A
INTENSITY (cts/s/100ma)
DIFF
2θ (deg)
b
$La_5Cu_5O_{13.35}$ 1.2015A
INTENSITY (cts/s/100ma)
DIFF.
2θ (deg)

TABLE 2
Metal–Oxygen Bond Distances in $La_5Cu_5O_{13.35}$ from Atomic Positions in Table 1b

Cu(1)–O(1)	2 at 1.92 Å	La(1)–O(3)	4 at 2.75 Å
–O(4)	2 at 2.00 Å	–O(3′)	4 at 2.84 Å
–O(4′)	2 at 2.09 Å	–O(5)	2 at 2.83 Å
	(mean = 2.00 Å)	–O(5′)	2 at 2.81 Å
			(mean = 2.80 Å)
Cu(2)–O(3)	1 at 2.13 Å	La(2)–O(1)	1 at 2.64 Å
–O(3′)	1 at 1.98 Å	–O(3)	2 at 2.58 Å
–O(4′)	1 at 2.02 Å	–O(4)	2 at 2.89 Å
–O(5)	2 at 1.92 Å	–O(4′)	2 at 2.44 Å
	(mean = 1.99 Å)	–O(5)	1 at 2.68 Å
		–O(5′)	1 at 2.57 Å
		–O(5′)	1 at 3.07 Å
			(mean = 2.68 Å)
Cu(2′)–O(3)	1 at 1.99 Å	La(2′)–O(1)	1 at 2.64 Å
–O(3′)	1 at 2.14 Å	–O(3′)	2 at 2.51 Å
–O(4′)	1 at 2.00 Å	–O(4)	2 at 2.48 Å
–O(5′)	2 at 1.92 Å	–O(4′)	2 at 2.94 Å
	(mean = 1.99 Å)	–O(5)	1 at 2.58 Å
		–O(5)	1 at 3.04 Å
		–O(5′)	1 at 2.69 Å
			(mean = 2.68 Å)

Note. Estimated errors are about 0.02 Å.

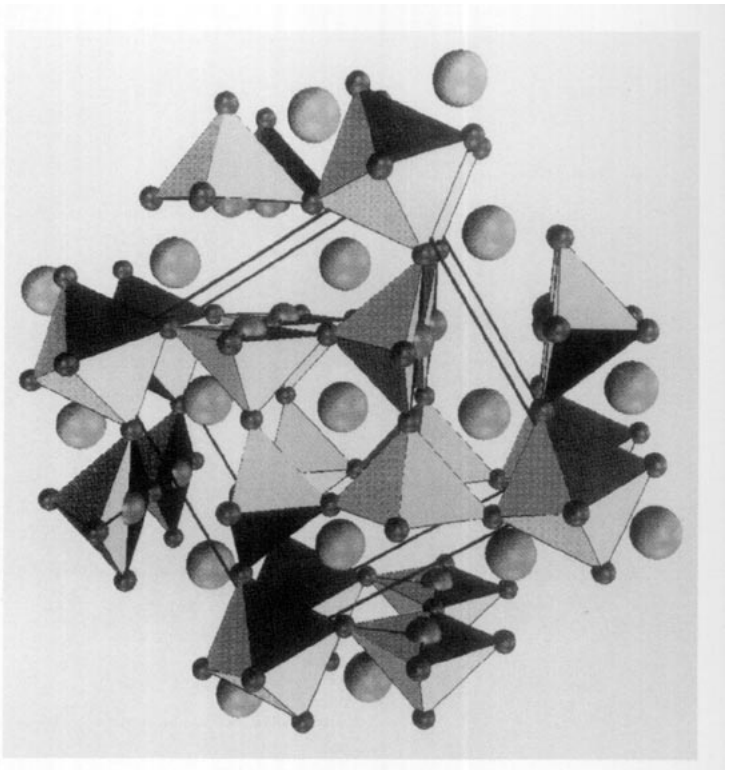

FIG. 3. A polyhedral representation of the structure of $La_5Cu_5O_{13}$ viewed approximately 15° off the *b*-axis. Two perovskite slabs are shown and the unit cell is outlined. Lanthanum atoms are represented by large spheres, copper by medium spheres at center of polyhedra, and oxygen by small spheres.

coprecipitated hydroxides of both La and Cu were also unsuccessful. Apparently $La_5Cu_5O_{13+\delta}$ can be prepared only by careful reduction of the higher valent $LaCuO_3$. These results indicate that $La_5Cu_5O_{13+\delta}$ may be metastable with respect to La_2CuO_4 and CuO at ambient pressure in the temperature range studied. Indeed we have found that $La_5Cu_5O_{13+\delta}$ could be prepared directly from the binary oxides only under high oxygen pressures. These facts underscore the utility of high oxygen pressure syntheses (1, 3) for preparing unique oxygen-defect cuprates.

The final positional and isotropic thermal parameters for $La_5Cu_5O_{13.35}$ given in Table 1 were used to calculate selected bond distances and angles in Table 2. A polyhedral representation of the structure of $La_5Cu_5O_{13}$ is shown in Fig. 3. $La_5Cu_5O_{13}$ is derived from its parent tetragonally distorted perovskite, $LaCuO_{3-\delta}$, through an ordering of oxygen vacancies in the (0*k*0) planes. This ordering is complete at $\delta = 0.40$ and creates a unit cell which is related to the original Perovskite subcell by $a = \sqrt{5} \times a_p$, $b = a_p$, and $c = \sqrt{5} \times a_p$. In fact, all of the unique oxygen orderings observed in the $LaCuO_{3-\delta}$ system can be approximately described by their relation to the parent perovskite lattice parameter as given in Table 3. The unique ordering of oxygen atoms in $La_5Cu_5O_{13}$ creates one-dimensional channels of vacancies which run parallel to the *b*-axis, which are clearly visible in Fig. 3. $La_5Cu_5O_{13+\delta}$ is nearly isostructural with $BaLa_4Cu_5O_{13}$ (7) and consists of one distorted CuO_6 octahedron with Cu–O distances of 1.915, 1.998, and 2.078 Å and four distorted CuO_5 square pyramids with Cu–O distances ranging from 1.917–2.140 Å, per crystallographic unit cell. Each unit cell also contains one 12-coordinate La atom and four 10-coordinate La atoms. The Cu–O–Cu bond angles are slightly distorted from their ideal value of 180°. This distortion is a result of the mismatch of the La–O and Cu–O layers which comprise these complex oxygen-defect perovskites. As noted by Michel *et al.* (7), insertion of the extra oxygen into the O(2) sites gives an unrealistically short Cu(2)–O(2) distance of 1.63 Å. In these regions, the surrounding atoms presumably relax toward their ideal positions and create a more octahedral-like coordination for the neighboring Cu(2) atoms.

TABLE 3
Crystallographic Unit Cells Related to Perovskite Cells (a_p)

N	Formula	Cell
1	$LaCuO_3$	$a_p \times a_p \times a_p$
5	$La_5Cu_5O_{13}$	$\sqrt{5}a_p \times a_p \times \sqrt{5}a_p$
2	$La_2Cu_2O_5$	$\sqrt{2}a_p \times 2\sqrt{2}a_p \times a_p$

It is interesting to note that the formal average oxidation state of Cu is +2.34 in $La_5Cu_5O_{13.35}$. This is essentially identical to the formal average oxidation state of copper in the well-known 90 K superconductor $YBa_2Cu_3O_7$. However, as noted earlier, $La_5Cu_5O_{13.35}$ is metallic but *not* superconducting. In fact, we have not observed superconductivity for any value of δ in the $LaCuO_{3-\delta}$ system. This fact is apparently due to the three-dimensional nature of the structures of the various oxygen ordering schemes in $LaCuO_{3-\delta}$. Many authors have pointed out that all of the high-temperature superconducting cuprates contain two-dimensional copper–oxygen planes. The magnetic and transport properties of $LaCuO_{3-\delta}$ for $\delta = 0.0$–0.5 have been described in detail by Bringley *et al.* (3).

A unique feature of the $LaCuO_{3-\delta}$ system is the relationship between the formal oxidation state of copper and the coordination geometry about the copper atoms. For $\delta = 0.0$ ($LaCuO_3$), the formal oxidation state of copper is +3.0 and every copper is octahedrally coordinated, while for $\delta = 0.5$ the formal oxidation state of copper is +2.0 and every copper is square pyramidally coordinated. For δ between 0 and 0.5 then, by definition, the number of holes (or Cu^{3+}) will be equal to the number of copper atoms in octahedral coordination. This empirical relationship may suggest a model in which the holes generally reside at the octahedrally coordinated copper. Additional light on this oversimplified model might be shed by calculating the bond valences and their corresponding sums (11) at the various copper atom positions for each unique oxygen ordering in the $LaCuO_{3-\delta}$ system. The calculation of bond valences sums has been described in detail by Brown and Altermatt (12). Using Brown's values of $B = 0.37$ and $R_0 = 1.679$ (11), the bond valence sum model correctly predicts a valence of Cu(+3.02) in $LaCuO_3$. However, the bond valence sum yields a valence of Cu(+2.19) for Cu in $La_2Cu_2O_5$. For $La_5Cu_5O_{13.35}$, the bond valence sums yield a valence of Cu(+2.6) for copper in octahedral sites and Cu(+2.17–2.19) for copper in square-pyramidal sites. Although the calculated bond valence sums are in qualitative agreement with the above model and seem to suggest a localization of holes at octahedrally coordinated Cu in $La_5Cu_5O_{13+\delta}$, this description is probably not particularly useful for the $LaCuO_{3-\delta}$ perovskites since, as pointed out by Brown (11), the copper oxides are among the classes of compounds for which the valence sum rule does not hold, and more importantly, $La_5Cu_5O_{13+\delta}$ is metallic so that a localized ionic model is inappropriate.

ACKNOWLEDGMENTS

The authors thank Richard F. Boehme for assistance in collecting diffraction data and Steven S. Trail for assistance with sample preparations. D.E.C. was supported by the U.S. Department of Energy, Division of Materials Sciences under Contract DE-AE02-76CH00016.

REFERENCES

1. J. F. Bringley, B. A. Scott, L. J. La Placa, R. F. Boehme, T. M. Shaw, M. W. McElfresh, S. S. Trail, and D. E. Cox, *Nature (London)* **347,** 263 (1990).
2. J. G. Bednorz and K. A. Mueller, *Z. Phys. B* **64,** 189 (1986).
3. J. F. Bringley, B. A. Scott, S. J. La Placa, F. Mehran, T. R. McGuire, M. W. McElfresh, and D. E. Cox, *Phys. Rev. B.* **47,** 15269, (1993).
4. S. Darracq, A. Largeteau, G. Demezeau, B. A. Scott, and J. F. Bringley, *Eur. J. Solid State Inorg. Chem.* **29,** 585 (1992).
5. K. R. Poeppelmeier, M. E. Lebnowicz, J. C. Scanlon, J. M. Longo, and W. B. Yelon, *J. Solid State Chem.* **45,** 71 (1982).
6. S. J. La Placa, J. F. Bringley, B. A. Scott, and D. E. Cox, *Acta Crystallogr. C* **49,** 1415 (1993).
7. C. Michel, L. Er Rahko, M. Hervieu, J. Pannetier, and B. Raveau, *J. Solid State Chem.* **68,** 143 (1987).
8. A. I. Nazzal, V. Y. Lee, E. M. Engler, R. D. Jacowitc, R. D. Tokura, and J. B. Torrance, *Physica C* **153–155,** 1367 (1988).
9. H. M. Rietveld, *J. Appl. Crystallogr.* **2,** 65 (1969); A. E. Hewat, AERE Harwell, Report No. R7350 (1973).
10. W. A. Dollase, *J. Appl. Crystallogr.* **19,** 267 (1986).
11. I. D. Brown, *Physica C* **169,** 105 (1990).
12. I. D. Brown and D. Altermatt, *Acta Crystallogr. B* **41,** 244 (1985).