Crystal structure of the high-temperature superconductor $La_{1.85}Sr_{0.15}CuO_4$ above and below T_c

R. J. Cava

AT&T Bell Laboratories, 600 Mountain Avenue, Murray Hill, New Jersey 07974

A. Santoro

National Bureau of Standards, Gaithersburg, Maryland 20899

D. W. Johnson, Jr. and W. W. Rhodes

AT&T Bell Laboratories, Murray Hill, New Jersey 07974

The crystal structure of $La_{1.85}Sr_{0.15}CuO_4$ has been determined at 300, 60, and 10 K by neutron-diffraction powder profile analysis. The structure is of the tetragonal K_2NiF_4 type at ambient temperature, but undergoes an orthorhombic distortion near 200 K which buckles the copper-oxygen planes. The crystal structure of the orthorhombic phase is not significantly different above and below T_c. The copper-oxygen coordination polyhedron changes shape in a subtle manner at the tetragonal-to-orthorhombic phase transition, but is unchanged at T_c.

Since the report of possible high-T_c superconductivity in a mixture of compounds in the La-Ba-Cu-O chemical system,[1] these and similar materials have been studied extensively. The superconducting component of the compound mixture was later identified as having stoichiometry $La_{2-x}Ba_xCuO_{4-y}$ in the tetragonal K_2NiF_4 structure type.[2] Further studies found bulk superconductivity to occur at higher temperatures, on the order of 40 K, in the Sr analog $La_{2-x}Sr_xCuO_{4-y}$,[3-5] for x near 0.15. The synthetic conditions influence the charge compensation (on M^{2+} for La^{3+} substitution) due to the balance between the oxidation of Cu^{2+} to Cu^{3+}, and the amount of oxygen deficiency. Theoretical studies have shown that the density of electronic states at the Fermi level is comprised of a mixture of contributions from copper d and oxygen p states,[6,7] and that a breathing mode of the copper-oxygen polyhedron may couple to these states and give rise to the high T_c's. The $La_{2-x}Sr_xCuO_4$ compounds have been shown to undergo a second-order structural phase transition from tetragonal to orthorhombic symmetry on cooling.[8] The phase transition is at approximately 200 K for $x=0.15$. In this Rapid Communication we present the results of structural studies at 300, 60, and 10 K of $La_{1.85}Sr_{0.15}CuO_4$ (bulk $T_c=37.5$ K) as determined by neutron diffraction powder profile analysis. Compounds of this stoichiometry are very close to the optimal composition for the best superconducting properties.[5,9] The results described here show that the orthorhombic distortion involves buckling of the copper-oxygen planes, with a subtle change in the shape of the Cu-O coordination polyhedron. No significant structural changes are found to occur between normal and superconducting states at 60 and 10 K, respectively.

The material for the powder diffraction study was prepared from a mixture of $SrCO_3$, CuO, and $La_2(CO_3)_3$, ball milled, filtered, dried, and fired for 2 h in air at 900 °C, and ball milled, filtered, and redried. The powder was then fired at 1000 °C for one day and 900 °C in flowing O_2 for one day and cooled slowly to room temperature

in the gas stream. Powder x-ray diffraction showed the material to be of the tetragonal K_2NiF_4 type at room temperature, with good crystallinity, and also showed the presence of 3–5% of a perovskitelike phase often reported to be present in ceramic preparations. The neutron diffraction measurements were performed on the high-resolution five-counter powder diffractometer at the National Bureau of Standards, employing neutrons of wavelength 1.5480 Å. The data were collected with a 10' in-pile collimator, a 20' monochromatic beam collimator, and a 10' diffracted beam collimator, in the angular range 12–113° (2θ). The portions of the diffraction pattern containing diffraction peaks from the aluminum sample container and the very small amount of chemical impurity were omitted from the refinement. The powder profile refinement was performed using the Rietveld program[10] adapted to the five-detector diffractometer design and modified to allow the refinement of background intensity.[11] The peak profiles from $La_{1.85}Sr_{0.15}CuO_4$ were described well by the standard Gaussian function. The neutron scattering amplitudes employed were $b(La)=0.827$, $b(Sr)=0.702$, $b(Cu)=0.772$, and $b(O)=0.581$ ($\times 10^{-12}$ cm). In the final refinement of the structural models, all structural, lattice, and profile parameters were refined simultaneously. Refinements were terminated when in two successive cycles the weighted agreement factor R_{WP} varied by less than one part in a thousand.

The final structural parameters are presented in Tables I and II. The ambient temperature crystal structure (Table I) has tetragonal symmetry, space group $I4/mmm$, and is of the undistorted K_2NiF_4 type. The excellent agreement value for Bragg intensities alone ($R_N=3.71$), and the ratio of the weighted total profile agreement to the agreement expected from statistics alone ($R_{WP}/R_E = \chi = 1.32$) attest to the high quality of the fit. Lanthanum and strontium atoms were distributed randomly in one type of site. Although short-range order of La and Sr cannot be excluded based on the powder data, long-range order does not occur, as that would be visible through the

TABLE I. The crystal structure of $La_{1.85}Sr_{0.15}CuO_4$ at 300 K. Space group: $I4/mmm$. $a_0 = 3.7793(1)$, $c_0 = 13.2260(3)$, $R_N = 3.71$, $R_P = 7.15$, $R_{WP} = 9.75$, $R_E = 7.40$, $\chi = 1.32$.

Atom	Position	x	y	z	B
La/Sr	$4e$	0.0	0.0	0.36046(10)	0.48(2)
Cu	$2a$	0.0	0.0	0.0	0.42(3)
O1	$4e$	0.0	0.0	0.1824(1)	1.33(3)
O2	$4c$	0.0	0.5	0.0	0.78(3)

appearance of additional peaks in the diffraction pattern. Oxygen-ion designations [e.g., O(1), O(2)] are assigned according to the conventional labeling. In the final refinement, six structural and 17 profile parameters (including a_0 and c_0) were varied.

The crystal structure at 60 and 10 K has orthorhombic symmetry. The diffraction data are not consistent with a face centered lattice, due to the presence of a number of weak reflections which violate the systematic absences required by the lattice. Refinements were therefore carried out in a number of subgroups of $Fmmm$, specifically $Cmmm$, $Cmm2$, and $Cmca$. Of these, the last gave the best fit to the measured intensities. Additional refinements were attempted using the symmetry of those subgroups of $Cmca$ which provide two inequivalent sites for the Cu ions, i.e., $Pmcb$ and $Pmna$. The results of these calculations were not significantly better than those obtained for $Cmca$, and therefore we assumed this to be the space group describing the symmetry of the low temperature phase. The structural results are presented in the

TABLE II. The crystal structure of $La_{1.85}Sr_{0.15}CuO_4$ at 60 and 10 K. Space group: $Bmab$.

Atom Position	60 K	10 K
La/Sr $8f(0,y,z)$		
y	-0.004955(10)	-0.004964(9)
z	0.36072(3)	0.36077(2)
B	0.278(4)	0.281(5)
Cu $4a(0,0,0)$		
B	0.223(6)	0.214(6)
O1 $8f(0,y,z)$		
y	0.0256(1)	0.0255(1)
z	0.18257(7)	0.18260(6)
B	0.662(7)	0.656(7)
O2 $8e(0.25,0.25,z)$		
z	0.00560(6)	0.00573(6)
B	0.435(9)	0.399(9)
a_0	5.3252(1)	5.3240(1)
b_0	5.3546(1)	5.3547(1)
c_0	13.1844(1)	13.1832(1)
R_N	3.42	3.41
R_P	5.20	5.22
R_{WP}	7.60	7.59
R_E	4.27	4.23
χ	1.78	1.79

nonstandard setting of this space group, $Bmab$ $(b > a)$, to facilitate the direct comparison between the undistorted and distorted K_2NiF_4 structure types.[12,14] The orthorhombic distortion causes a doubling in the volume of the crystallographic unit cell, with the relation between the orthorhombic (O) and tetragonal (T) cells given by $(a,b,c)_O = (1,1,0/-1,1,0/0,0,1)(a,b,c)_T$. The final structural parameters are presented in Table II for 60 and 10 K. The crystal structures are again very well determined, as can be seen by inspection of the agreements for Bragg intensities alone (3.42 and 3.41%) and χ values (1.78 and 1.79) at 60 and 10 K, respectively. Comparison of the coordinates with those in Table I indicates the similarity among the structures. At all three temperatures, the thermal parameter for the O(1) atom is considerably larger than that for the O(2) atom. This may be due to (a) a relatively large thermal vibration of this atom, (b) a static disorder in the position of this atom without long-range coherence, or (c) an oxygen occupancy in this site which is smaller than that expected, e.g., oxygen vacancies. To test for the latter possibility, the 10 K data were employed in a refinement in which the occupancy of this site (normally set equal to 1) was allowed to vary. The refinement converged to an occupancy value of 1.0004(40), indicating that within the precision of the refinement, oxygen vacancies are not present in significant amounts in $La_{1.85}Sr_{0.15}CuO_{4-y}$ (e.g., $y \approx 0$) prepared as described. Charge compensation for the Sr substitution has therefore been accomplished essentially entirely by oxidation of Cu^{2+} to Cu^{3+}. Such oxygen vacancies were also not unambiguously observed in a powder neutron diffraction study of the Ba analog of this compound.[13] Single-crystal neutron diffraction measurements will be necessary to refine further the structural aspects of the possible oxygen nonstoichiometry.

A general representation of the tetragonal crystal structure is presented in Fig. 1. On the scale of the figure, the orthorhombic and tetragonal structures are not distinguishable, except that the orthorhombic crystallographic until cell is twice the area in the plane perpendicular to c. The perovskitelike planes of CuO_6 "octahedra" are emphasized to illustrate the highly two-dimensional nature of the planes (perpendicular to c) in which the strong copper-oxygen [O(2)] orbital overlap occurs. These copper-oxygen planes are separated by planes of (La and Sr)-O(1) in an NaCl (100) plane-type arrangement. The copper atoms in one plane do not share oxygens with copper atoms in other planes. The oxygen atoms in the copper-oxygen plane [O(2)] are bonded to two copper atoms within the planes, but are also bonded to four La and Sr atoms in adjacent planes.

It is the nature of the copper-oxygen bonding in the superconducting materials of this structure type which is in part responsible for their high-T_c superconductivity.[6] Of particular importance are the four short Cu-O distances (1.889 Å) within the infinite Cu-O planes, and the two long distances (2.411 Å) perpendicular to the planes. Similar Cu-O separations have been observed in the Ba analog.[13] The short in-plane Cu-O distances are indicative of the strong copper-d oxygen-p orbital overlap, which in this case occurs at the Fermi level E_F.[6] Varia-
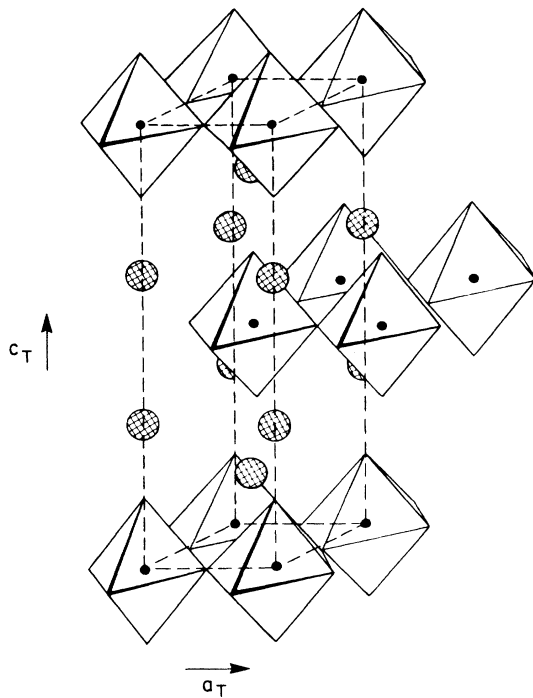
FIG. 1. Generalized view of the highly two-dimensional tetragonal $La_{1.85}Sr_{0.15}CuO_4$ structure. La and Sr atoms, large shaded circles; Cu atoms, small filled circles. Oxygen atoms at vertices of polyhedra: O(2) atoms at vertices within Cu-O planes (perpendicular to c), O(2) atoms at vertices between these planes. The CuO_6 "octahedron" is severely elongated parallel to c.
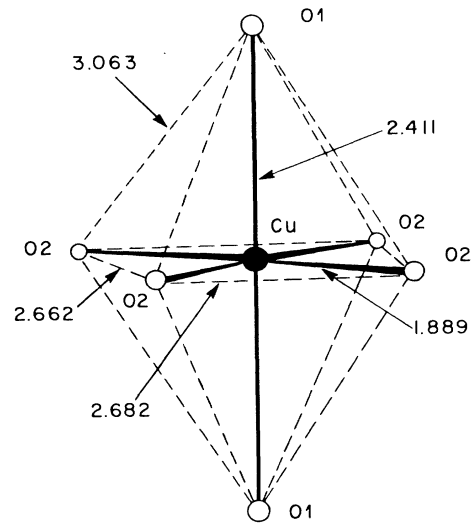

FIG. 2. Copper-oxygen coordination in $La_{1.85}Sr_{0.15}CuO_4$ at 10 K. Solid lines, copper-oxygen bonds; dashed lines, oxygen polyhedron. Atom separations in angstroms.

tions of the copper-oxygen coordination observed in these materials are found in many copper (+2) oxides.[15] They are generally either strictly square planar (only four oxygen neighbors) or of the 4+1 square pyramidal, or 4+2 distorted bipyramidal geometries. The copper-oxygen coordination polyhedron found for $La_{1.85}Sr_{0.15}CuO_4$ at 10 K is shown in Fig. 2. The elongation of the bipyramid is apparent. The important interatomic separations and angles for this polyhedron are presented in Table III. The copper-oxygen bond lengths are independent of tempera-

ture between 300 and 10 K. The shape of the copper-oxygen bipyramid changes in a subtle manner on going from the tetragonal to the orthorhombic phase. The shape of the base changes from square, with four equal O(2)-O(2) separations at 300 K of 2.6723(1) Å, to rectangular, with two O(2) separations of 2.6620(1) Å and two of 2.6816(1) Å. The very small difference, 0.02 Å, is statistically highly significant, at 200 standard deviations. The four Cu-O(2)-Cu angles change from 90° to two sets of 89.58(1)° and 90.42(1)°. It is not known at the present time whether these very small differences in the copper coordination in the tetragonal and orthorhombic phases
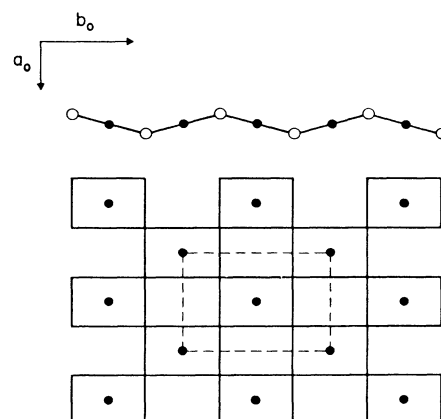
TABLE III. Bond lengths and angles in the copper-oxygen polyledron in $La_{1.85}Sr_{0.15}CuO_4$.

	300 K	60 K	10 K
Cu-O(1) (×2)	2.4124(5)	2.4110(9)	2.4112(8)
Cu-O(2) (×4)	1.8896(1)	1.8894(1)	1.8893(1)
O(2)-O(2) (×4)	2.6723(1)		
(×2)		2.6814(1)	2.6816(1)
(×2)		2.6626(1)	2.6620(1)
O(2)-O(1) (×4)	3.0644(4)	3.063(2)	3.063(1)
Cu-Cu	3.7793(1)	3.7759(1)	3.7755(1)
O(2)-Cu-O(2)	90.0	89.58(1)	89.58(1)
		90.42(1)	90.42(1)
O(2)-Cu-O(1)	90.0	89.9(1)	89.9(1)
Cu-O(2)-Cu	180.0	175.4(2)	175.4(2)

FIG. 3. The distortion of the copper-oxygen layer in $La_{1.85}Sr_{0.15}CuO_4$ at 60 and 10 K. Lower figure demonstrates direction and orientation of "square" planar copper-oxygen coordination elongation: copper, filled circles; oxygen [O(2)] at corners of rectangles; unit cell, dashed lines. Upper figure illustrates the accordianlike buckling of the layer parallel to b; oxygen atoms, open circles. Both the elongation and buckling angle have been exaggerated for purposes of illustration.

TABLE IV. Metal-oxygen bond lengths in the (lanthanum-strontium)-oxygen polyhedron in $La_{1.85}Sr_{0.15}CuO_4$.

	300 K	60 K	10 K
La—O(1)(×1)	2.3557(1)	2.3545(1)	2.3545(1)
O(1)(×4)	2.732(1)		
(×2)		2.7253(1)	2.7250(1)
(×1)		2.5776(1)	2.5784(1)
(×1)		2.8978(8)	2.897(2)
O(2)(×4)	2.6409(3)		
(×2)		2.597(2)	2.595(2)
(×2)		2.6726(1)	2.6731(1)
Average La—O	2.650	2.647	2.646

FIG. 4. Ninefold lanthanum-and-strontium oxygen coordination in $La_{1.85}Sr_{0.15}CuO_4$ at 10 K, with atom separations in angstroms. O(2) atoms are in the copper-oxygen planes and are also bonded to two Cu atoms.

reflect in any way a significant change in the electronic configuration of the atoms. There is no significant change in shape or size of the Cu-O coordination polyhedron on going through T_c.

The major change in the structure in the tetragonal to orthorhombic phase transition involves the buckling of the copper-oxygen bipyramidal planes. This accordionlike buckling involves small rigid rotations of the bipyramids about axes parallel to a, through the shared oxygen [O(2)] atoms. The distortion is illustrated in Fig. 3. The O(2)—Cu—O(2) bond angles are changed from 180° in the tetragonal phase to 175.4(2)° in the orthorhombic phase. As the Cu—O(2) bonding is directly involved at E_F, this change in bond angle may be more significant than the small change in shape of the polyhedron.

Lanthanum and strontium are nine-coordinated to oxygen (Table IV) in both tetragonal and orthorhombic structures. The shape of the polyhedron is that of a square antiprism with one capped face, with the La and Sr displaced considerably from the antiprism center toward the capped face. This coordination in the orthorhombic structure at 10 K is shown in Fig. 4. The figure shows that the (La and Sr)-O(1) "planes" perpendicular to c are actually puckered. The same is true in the tetragonal phase. The La and Sr atoms need not occupy exactly the same position within this polyhedron. Such a displacively disordered atomic arrangement would manifest itself as a relatively large thermal parameter for the La and Sr atoms in the refinement, which is not the case. The relatively large thermal parameter for the O(1) atom may, however, reflect a small difference in its position dependent on the local ratio of La and Sr atoms bonded to it. The La and Sr atoms are equally strongly bonded to the oxygen atoms only weakly bonded to Cu [O(1)], and those involved in the Cu-O conducting planes [O(2)]. Thus the nature of the atom on this site may strongly influence the Cu—O(2) bonding. This suggests a microscopic reason for the strong influence of the La site substitutions on T_c. The shape of the La and Sr oxygen polyhedron is somewhat different in the tetragonal and orthorhombic structures with two bond lengths [to O(1)] considerably altered. Bond lengths to O(2) atoms are also different, but the average (La and Sr)—O bond length
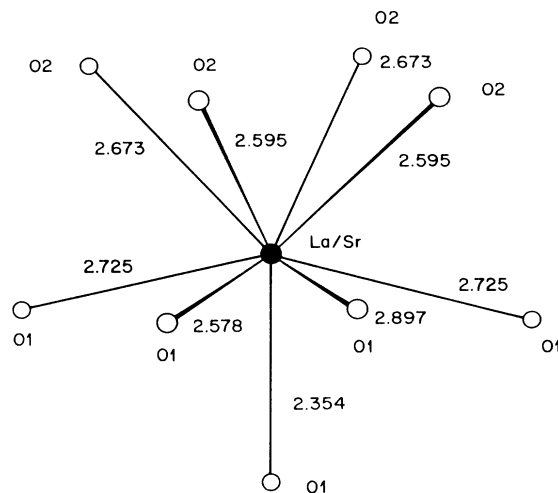
seems only to decrease smoothly with temperature. There is no change in the La and Sr oxygen coordination at T_c.

The neutron diffraction powder profile analysis technique has allowed us to describe the structure of the high T_c superconductor $La_{1.85}Sr_{0.15}CuO_4$ in considerable detail. The structural changes which occur at the tetragonal to orthorhombic phase transition have been specified. We do not find significant structural changes at T_c within the precision of the measurements. The structural data provide a basis for the interpretation of the wealth of experiments which probe the microscopic aspects of the properties of these materials. In particular, we have emphasized the two-dimensional nature of the crystal structure, and the interesting copper-oxygen coordination. The crystal structure we have determined for orthorhombic $La_{1.85}Sr_{0.15}CuO_4$ is very similar to that reported for La_2CuO_4.[13] In neither case has the structural distortion characteristic of the charge-density wave (CDW) predicted for undoped La_2CuO_4 (Ref. 6) been observed. The structural distortions associated with CDW's generally give rise to extremely weak diffraction effects which are not observable in conventional diffraction measurements, and therefore the possible extence of the CDW has not yet been addressed from a structural point of view. A large body of crystal-chemical knowledge has been accumulated in recent years for oxides of this structure type in a different context (see Refs. 12 and 14, and references therein), providing a groundwork on which further chemical study can be based.

[1] J. G. Bednorz and K. A. Müller, Z. Phys. B **64**, 189 (1986).

[2] H. Takagi, S. Uchida, K. Kitazawa, and S. Tanaka, Jpn. J. Appl. Phys. **26**, L123 (1987).

[3] K. Kishio, K. Kitazawa, S. Kanabe, I. Yasuda, N. Sugii, H. Takagi, S. Uchida, K. Fuki, and S. Tanaka, Chem Lett. (to be published).

[4] R. J. Cava, R. B. van Dover, B. Batlogg, and E. A. Rietman, Phys. Rev. Lett. **58**, 408 (1987).

[5] J. M. Tarascon, L. H. Greene, W. R. McKinnon, G. W. Hull, and T. H. Geballe, Science **235**, 1373 (1987).

[6] L. F. Mattheiss, Phys. Rev. Lett. **58**, 1028 (1987).

[7] W. Weber, Phys. Rev. Lett. **58**, 1371 (1987).

[8] R. M. Fleming, B. Batlogg, R. J. Cava, and E. A. Rietman (unpublished).

[9] R. B. van Dover, R. J. Cava, B. Batlogg, and E. A. Rietman, Phys. Rev. B **35**, 5337 (1987).

[10] H. M. Rietveld, J. Appl. Cryst. **2**, 65 (1969).

[11] E. Prince, in *U. D. Technical Note 1117,* edited by F. J. Shorten (National Bureau of Standards, Washington, DC, 1980),

[12] K. K. Singh, P. Ganguly, and J. B. Goodenough, J. Solid State Chem. **52**, 254 (1984).

[13] J. D. Jorgensen, H.-B. Schuttler, D. G. Hinks, D. W. Capone II, K. Zhang, and M. B. Brodsky, Phys. Rev. Lett. **58**, 1024 (1987).

[14] P. Ganguly and C. N. R. Rao, J. Solid State Chem. **53**, 193 (1984).

[15] A. F. Wells, *Structural Inorganic Chemistry* (Clarendon, Oxford, 1984).