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THE CRYSTAL STRUCTURE OF SUPERCONDUCTING $La_2CuO_{4.032}$ BY NEUTRON DIFFRACTION

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The crystal structure of superconducting (37.5 K) $La_2CuO_{4.032}$ has been refined from single-crystal neutron-diffraction data at room temperature and 15 K. At both temperatures it exhibits the orthorhombic symmetry Cmca. The extra oxygen O4 atoms occupy the special positions ($\frac{1}{4}$ y $\frac{1}{4}$ with $y=0.243$ at 15 K). They are located between two successive LaO layers and are surrounded by distorted cubes built up of two interpenetrated tetrahedra, one comprising four La atoms and the other four O1 atoms (the apical oxygen atoms of the CuO_6 octahedra). The O4 insertion causes a 0.75 Å displacement of 4.8% of the O1 atoms towards new O3 positions ($x=0.030(5)$, $y=0.182(2)$, $z=0.100(5)$). From the refined values of the occupancy factors at 15 K, it is deduced that for each extra O4 three O1 are displaced to O3 with one short O3–O4 distance of 1.64(3) Å. This value indicates the formation of a strong O–O covalent bond of peroxide type with a formal 2-valence. Since the La and Cu sublattices have been found to be fully occupied and the doping does not change the oxygen charge, the La, Cu, and O sublattices have the formal valences 6+, 2+, and 8−, respectively. However, the increase in La coordination and the consequent La–O distance readjustment indicate, when compared to the undoped compound structure, that a charge transfer occurs in $La_2CuO_{4.032}$, with the excess positive charge going either to the La or to the O sublattice. In the latter case it would correspond to the formation of holes in the O 2p band.

1. Introduction

It is well established today that La_2CuO_4 becomes superconducting with T_c's between 28 K and 40 K either by cation doping on the La-sites or by raising the oxygen content to more than 4. The superconducting properties of "undopped" La_2CuO_4, synthesized under high oxygen pressure, were first reported by Beille et al. [1]. This publication was followed by several others on undoped La_2CuO_4 samples synthesized under slightly different oxygen-rich conditions [2,3]. Samples of $La_2CuO_{4+\delta}$ with somewhat appreciable Meissner effects were obtained reproducibly by Schirber et al. [4] and by Demazeau et al. [5], who carried out the synthesis under high oxygen pressure (a few kbar) at high temperature (500–800°C).

Schirber et al. [4] determined the formula of their oxygen-excess superconducting samples, $La_2CuO_{4+\delta}$, by electron microprobe analysis, iodometric titration and thermogravimetric analysis. The first showed that the La/Cu ratio was 2:1 with an estimated uncertainty of 1%. The iodometric titration and the thermogravimetric analysis yielded $\delta=0.032$ and $\delta=0.13$, respectively. In order to reconcile the difference in oxygen stoichiometry Schirber et al. concluded that the excess oxygen is incorporated in the structure as a superoxide ion, O_2^-, and that the approximate bulk stoichiometry of their superconducting sample was $La_2CuO_{4.13}$. Subsequent X-ray photoemission spectroscopy results of Rogers et al. [6] confirmed this interpretation. Recently Zhou et al. [7] have shown that an $La_2CuO_{4+\delta}$ sample with $\delta=0.05$ (determined by iodometric titration) loses all its oxygen in a first order phase change near 250°C in N_2. This phase change is accompanied by a tran-

sition from a superconducting state to an antiferromagnetic one. Zhou et al. also observed that excess superficial oxygen is lost progressively over a large temperature range. These data make it unnecessary to postulate the presence of bulk superoxide corresponding to $\delta = 0.13$. They also indicate that any superoxide identified by XPS is probably associated with superficial oxygen.

By using neutron powder diffraction techniques Jorgensen et al. [8] showed that superconducting samples of $La_2CuO_{4+\delta}$ consist of two nearly-identical orthorhombic phases. The first has a stoichiometry close to La_2CuO_4 while the second is an oxygen-rich superconducting phase. The amount of the second phase in a given sample increases with the oxygen pressure at which the sample is annealed. Neutron diffraction measurements as a function of temperature show that the phase separation occurs reversibly near 320 K. The extensive overlap of the diffraction peaks corresponding to the two phases and the impossibility of producing samples entirely in the superconducting phase, made a unique determination of the structure impossible.

Because of the uncertainties about the position and the bonding of the excess oxygen in superconducting $La_2CuO_{4+\delta}$ samples, we have carried out the crystal structure determination of a superconducting $La_2CuO_{4.032}$ single crystal by neutron diffraction data taken at room temperature and 15 K.

2. Experimental

. The crystal synthesis and oxidation procedure have been described elsewhere [4,9]. In order to test its quality the single crystal to be used for the intensity data collection was mounted on a precession camera equipped with MoKα radiation ($\lambda = 0.7107$ Å). Because of the crystal dimensions only a small corner of the crystal was bathed by the X-ray beam. The doubling of most of the reflections clearly showed that the crystal was twinned. Shirane et al. [10] observed that La_2CuO_4 crystals comprise two types of microdomains related to each other by a rotation of 90° about the b axis. Moreover, these domains are equal in volume. As a result of this twin operation, $[010]_{90^\circ}$, each reciprocal node is occupied by two slightly split reflections, hkl and lkh. Another possible twin law is the pseudo symmetry plane operation $(110)_{tet}$ for which an hkl reflection is almost superposed with an lkh one. Our crystal contains only this latter twin law.

The lattice parameters at room temperature were determined from an X-ray powder film taken with a Guinier camera and $\lambda_{FeK\alpha}$ radiation. The powder sample was obtained by grinding a small fragment of the large single crystal used for neutron diffraction. Silicon powder was added as a standard. The values shown in table I are the result of a least-squares refinement.

The superconducting transition temperature for the single crystal was obtained by AC susceptibility measurements. The volume of superconducting phase was estimated to be about 70% with an onset at 37.5 K.

The neutron diffraction intensities were collected at room temperature and 15 K using the D9 four-circle diffractometer at the ILL reactor. The neutron wavelength was 0.48417 Å. This short value was chosen so that the two reflections around each node of the reciprocal lattice, coming from the two twin individuals were as close as possible. The crystal, whose dimensions were $2.5 \times 5 \times 1$ mm^3, was mounted on an aluminium pin. The intensities of ten of the strongest reflections were measured every 5 K on both sides of the superconducting transition temperature, namely between 50 K and 15 K. No measurable change, indicating a structural transition, was detected. The low temperatures were attained by the use of a close-cycle helium refrigerator (displex).

The lattice parameters and the orientation matrix were determined by least-squaring the previously centered angular settings of 20 reflections whose θ's were comprised between 24° and 39°. The intensities were measured using the $\omega/\chi\theta$ scan mode. The coupling factor curve was: $(\theta, \chi) \equiv (0.0, 0.0)$, $(15.0, 0.8)$, $(30.0, 1.2)$, $(50.0, 2.0)$, $(70.0, 2.0)$. A variable peak scan was used according to the following function: $(\theta, \text{scan width}) \equiv (1.0, 0.9)$, $(12.0, 0.8)$, $(24.0, 1.4)$, $(34.0, 1.8)$. The background was determined by measuring eight points (one every 0.15°) on each side of the peak. The alignment was checked by measuring the (202) reflection every 100 reflections. In order to check if the weak reflections were affected by multiple diffraction effects, some of the very weak ones were recorded using the Ψ scan mode. For all of them no significant change was observed

Table I
Crystallographic data.

	Lattice parameters		Space group Cmca; $\lambda = 0.48417$ Å
	room temperature	15 K	
	$a = 5.360(1)$ Å	$a = 5.350(1)$ Å	La: $0\,y\,z$
	$b = 13.181(6)$ Å	$b = 13.148(6)$ Å	Cu: $0\,0\,0$
	$c = 5.393(3)$ Å	$c = 5.398(3)$ Å	O1: $0\,y\,z$
			O2: $\frac{1}{4}\,y\,\frac{3}{4}$
			O3: $x\,y\,z$
			O4: $\frac{1}{4}\,y\,\frac{1}{4}$

	15 K	Room T.		15 K	Room T.
y La	0.36112(4)	0.36105(4)	U La 11	0.0052(7)	0.0091(6)
z La	0.0069(1)	0.0046(2)	U La 22	0.0028(2)	0.0053(1)
y O1	0.18302(8)	0.18290(8)	U La 33	0.0019(6)	0.0053(5)
z O1	$-0.0349(3)$	$-0.0243(5)$	U La 23	0.0003(2)	0.004(3)
y O2	$-0.00690(8)$	$-0.0051(1)$	U Cu 11	0.0033(11)	0.0001(7)
			U Cu 22	0.0046(3)	0.0099(2)
n O1	0.968(5)	0.943(4)	U Cu 33	0.0004(10)	0.0066(8)
n O2	0.993(4)	0.995(3)	U Cu 23	0.0001(3)	$-0.0002(5)$
			U O1 11	0.0106(7)	0.024(1)
$R_w(F^2)$	5.78%	5.03%	U O1 22	0.0042(3)	0.0057(3)
$R_{uw}(F^2)$	4.41%	3.33%	U O1 33	0.0125(5)	0.019(1)
χ^2	5.26	3.75	U O1 23	$-0.0012(4)$	$-0.0014(5)$
			U O2 11	0.0050(8)	0.0050(7)
			U O2 22	0.0096(3)	0.0165(4)
			U O2 33	0.0022(7)	0.0067(8)
			U O2 13	0.0007(3)	0.0020(2)

for Ψ varying between 20° and 180°. A total number of 1422 and 1073 reflections were measured at room temperature and 15 K, respectively. The intensities were converted into structure factors by the use of the ILL–COLL5 program.

3. Refinements and localization of the excess oxygen

The structural refinements were carried out by using the MXD program [11]. The $1/\sigma^2$ weighting scheme was used and those reflections for which $I < \sigma(I)$ were not taken into account. The neutron cross sections were: (b(La) $= 0.827$, b(Cu) $= 0.772$, and b(O) $= 0.581 \times 10^{-12}$ cm. The systematic absences corresponding to the Cmca space group are: for hkl, $h + k = 2n + 1$; for $h0l$, $l = 2n + 1$; and $hk0$, $h = 2n + 1$. The space group of the second individuals

is Acam and consequently the observed systematic absences for the two individuals are: $hk0$ for $h = 2n + 1$ and $k = 2n + 1$; $0kl$ with $k = 2n + 1$; $h0l$ with $h = 2n + 1$ and $k = 2n + 1$. If the twinning operation is only $(110)_{tet}$, the total intensity of each reciprocal node is given by $p_A I_{Ahkl} + p_B I_{Blkh}$ where p_A and p_B are the percentage of each individual in the crystal. Because of the systematic absences, the above sum is sometimes reduced to one term, the other being zero, which allows the determination of p, the other being $1 - p$. This parameter was refined together with the other variables and a value of 0.46 was obtained in the final refinement. At the beginning the four atoms of the asymmetric cell were placed in the following positions: La (8f) 0, y, z; Cu (4a) 0, 0, 0; O1 (8f) 0, y, z; O2 (8e) $\frac{1}{4}$, y, $\frac{1}{4}$. The starting positional parameters were those reported by Cava et al. for La$_{1.85}$Sr$_{0.15}$CuO$_4$ [12]. The introduction of the extinction correction did not yield any improvement

in the *R*-factors, therefore, we assumed it as negligible. At this stage the final refinement consisted in varying together the scale factor, the positional, the anisotropic thermal and occupancy parameters with the latter for the Cu cations fixed to unity. This yielded an occupancy factor of 1.00 for the La sites. Exactly the same results were obtained when the occupancy factor of Cu was varied and that of La fixed to unity. This strongly indicated that in this crystal the La/Cu ratio is exactly 2. The final results at this stage of the refinements for the room temperature and 15 K structures are given in table I. Note that there is no difference between the two structures. At low temperature the orthorhombicity is larger than at room temperature as the coordinates z_{La}, z_{O1}, and y_{O2} are further away from zero, the value which they would have if the crystal symmetry were tetragonal. Even at low temperature the two oxygen atoms exhibit anisotropic thermal parameters; the thermal ellipsoid of O2 is elongated along the *b* axis while that of O1 is contracted along the same axis.

Since the cation lattices do not comprise any vacancies, the structure must contain an excess oxygen. For locating it we used the low temperature data because in this case the thermal effects are minimized. As stated above in the MXD refinement program the total observed intensity associated to a given (*hkl*) node of the reciprocal lattice is compared to the calculated quantity $pI_{hkl} + (1-p)I_{lkh}$. Therefore, it is not too meaningful after the last cycle of refinement to calculate a difference Fourier map, unless the *p* coefficient is either far from 0.5 or determined independently. For the present crystal we obtained $p=0.46$. Besides, we knew a priori that this difference map should have only revealed small fractions of oxygen atoms. We chose to localize this oxygen excess from crystal chemical considerations and then try to refine its position.

By analogy to the structure of La₂NiO₄₊δ [13] an extra oxygen O3 was placed at $(\frac{1}{4} y \frac{1}{4})$. This position was also suggested by Zhou et al. [7] as a strong possibility for La₂CuO₄₊δ. A refinement, in which the *y* coordinate and the occupancy factor of O3 were varied together with all the other parameters mentioned above, was carried out. The O3 thermal parameter was fixed at $U=0.005$ Å. Convergence was attained after a few cycles and the $R(F^2)$ factor decreased from 5.78% to 5.61%. For O3 the following

values were obtained: $y_{O3}=0.243(4)$ and $p_{O3}=0.016(3)$. We tried then to vary the *x* and *z* coordinates of O3 together with the other parameters. The results of this refinement were quite unexpected because the O3 parameters changed drastically while all the others remained unchanged. The new values were: $x_{O3}=0.031(5)$, $y_{O3}=0.182(2)$, $z_{O3}=0.101(5)$, and $p_{O3}=0.023(2)\times2$. Since this position is just 0.75 Å from that of O1, it can only be occupied when O1 is empty. Therefore, O3 should not be interpreted as an excess oxygen, but the result of displacements of some of the O1 anions. The sum of O1 and O3 occupancy factors, 0.991(6), is indeed very close to unity. This clearly explains why the occupancy factor of O1 was found to be 0.943(5). The next cycle of refinement was carried out by keeping O3 in the new position and adding an excess oxygen O4 at $(\frac{1}{4} y \frac{1}{4})$ with *y* at 0.243. The positional parameters (including those of O3 and O4) and the thermal factors (except those of O3 and O4) of all atoms were varied together with the occupancy factors of O1, O3, and O4. With this model the *R* factor decreased from 5.31% to 5.14%. On the contrary, the refinement diverged when the *x* and *z* coordinates of O4 were varied. This indicates that the excess oxygen is in the special $(\frac{1}{4} y \frac{1}{4})$ position. The final results are given in table II.

The same procedure was applied to the room temperature data, the results are in agreement with the refinement based on the 15 K data; however, the larger thermal vibration masking the static displacements, did not allow an unambiguous conclusion.

4. Discussion

The structure of La₂CuO₄ is schematized in fig. 1a. For clarity only half cell ($a/2\times b\times c/2$) is shown. The Cu cations are located at the center of apically-elongated octahedra; the six Cu–O distances are Cu–O1 = 2.415(1) Å×2 and Cu–O2 = 1.9022 Å×4, with the two long distances along the *b* axis. The CuO₂ layers ae separated from each other by two LaO1 layers. Each layer is shifted of (1/2 0 1/2) with respect to the above and below layers so that the structure of La₂CuO₄ comprises the following sequence:

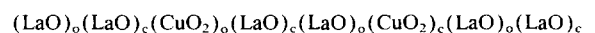(LaO)ₒ(LaO)c(CuO₂)ₒ(LaO)c(LaO)ₒ(CuO₂)c(LaO)ₒ(LaO)c

Table II

	Refinement 15 K			
y La	0.36111(4)		U La 11	0.0055(7)
z La	0.0069(1)		U La 22	0.0030(2)
y O1	0.18307(8)		U La 33	0.0022(6)
z O1	−0.0356(3)		U La 23	0.0002(2)
y O2	0.00697(7)		U Cu 11	0.0042(9)
x O3	0.030(5)		U Cu 22	0.0050(3)
y O3	0.182(2)		U Cu 33	−0.0001(8)
z O3	0.100(5)		U O1 11	0.0077(6)
y O4	0.243(4)		U O1 22	0.0040(3)
			U O1 33	0.0123(5)
n O1	0.943(5)		U O1 23	−0.0014(4)
n O2	0.993(4)		U O2 11	0.0055(7)
n O3	0.024(2)		U O2 22	0.0094(3)
n O4	0.016(2)		U O2 33	0.0023(6)
			U O2 13	0.0007(2)
$R_w(F^2)$	5.13%			
$R_{uw}(F^2)$	3.88%			
χ^2	4.20			

	Interatomic distances				
Cu–O1	2.415(1)	×2	O1–O2	3.061(1)	×2
Cu–O2	1.9022	×4		3.087(1)	×2
Cu–O3	2.46(2)	×2	O2–O2		
Cu–O4	3.72(4)	×4		2.6750(6)	×2
			O2–O3	2.7052(6)	×2
La–O1	2.352(1)	×1			
	2.537(2)	×1		2.76(3)	×2
	2.7417(3)	×2		2.87(3)	×2
	2.986(2)	×1		3.34(3)	×2
			O1–O4	3.47(3)	×2
La–O2	2.5923(8)	×2			
	2.6812(8)	×2	O3–O4	2.19(2)	×2
La–O3	2.27(3)	×2		2.02(2)	×2
	2.64(3)	×2			
	3.26(3)	×2		1.64(3)	×2
				2.43(3)	×2
La–O4	2.36(3)	×2		2.61(3)	×2
	2.43(3)	×2		1.89(3)	×2

The o and c subscripts indicate whether the cation is at the origin or the center of the mesh. The La cations are surrounded by nine oxygen atoms, four O1 at the same level, four O2 at the Cu level above (below), and one O1 from the La level below (above). The first eight oxygen atoms form an antiprism with the ninth capping the large square. The La cations are not located at the center of the antiprism, but are shifted toward the capping O1. The La–O distances are: La–O1 = 2.352(1) Å × 1, 2.537(2) Å × 1, 2.7417(3) Å × 2, 2.986(2) Å × 1 and LaO2 = 2.5923(8) Å × 2, 2.6812(8) Å × 2.

Figure 1b illustrates the modification that the structure undergoes after the introduction of the excess oxygen O4 atoms. These sites are located between two LaO1 layers which have the NaCl arrangement. Thus, the two LaO1 layers generate a layer of cubes whose corners are occupied by four La and four O1 atoms, each set of atoms forming a tetrahedron. The O4 atoms are located at the center of
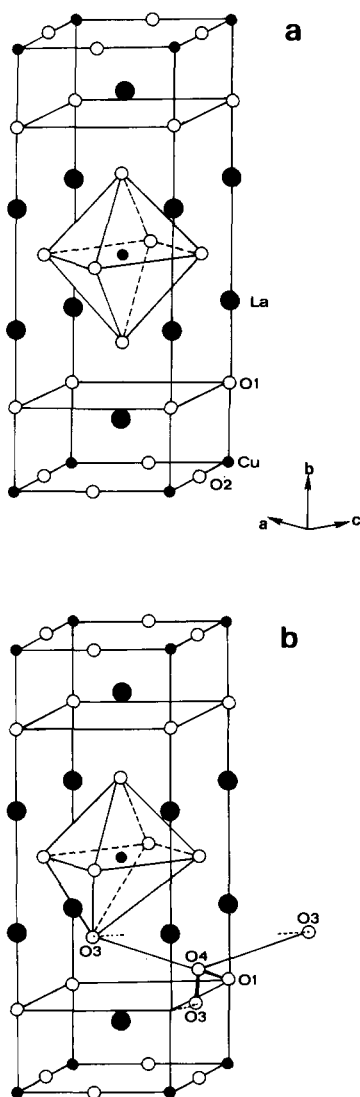
Fig. 1. (a) Three dimensional structural arrangement of La₂CuO₄. One tetragonal unit cell is represented. (b) The position of O4 in the pseudo tetragonal unit cell of La₂CuO₄.₀₃₂. The displaced O4 atoms to the O3 positions are indicated.

these cubes with an occupancy factor of 1.6%. Each time that an O4 site is occupied, four La cations become ten coordinated. The four La–O4 distances are 2.36(3) Å×2 and 2.43(3) Å×2. As shown by the structural refinement the La positions are not affected by he presence of the O4 excess oxygen. On the contrary, this excess oxygen brings about the dis-

placement of the O1 atoms toward the O3 sites. From the ratio of the occupancy factors of O3 and O4 it can be deduced that for each O4 three O1 are displaced to O3. The presence of O4 does not modify the Cu coordination (Cu–O4 = 3.72, 3.87 Å). However, it causes the distortion of three CuO₆ octahedra as for each octahedron one of the two apical oxygens gets off the b axis. The interatomic distances change only slightly, Cu–O1 = 2.415(1) Å becomes Cu–O3 = 2.46(2) Å.

As stated above each O4 is surrounded by four O1 atoms arranged as a tetrahedron (fig. 2). The list of all possible O1–O4, O3–O4 distances is: O1–O4 = 2.19(2) Å×2, 2.02(2) Å×2, O1–O3 = 1.64(3) Å×2, 1.89(3) Å×2, 2.43(3) Å×2, 2.61(3) Å×2. If each O4 is surrounded by three O3 and one O1, as the ratio of the occupancy factors seems to indicate, one of the O3–O4 distances must be 1.64 Å, the other three being either O4–O1 = 2.19 Å and O4–O3 = 2.61×2, or O4–O1 = 2.19 Å and O4–O3 = 2.43 Å×2. The short distance (1.64 Å) is indicative of a strong covalent bond and corresponds to the formation of an $(O_2)^{-2}$ peroxide grouping. The values found in peroxide compounds such as BaO_2 is about 1.5 Å [14], whereas the O–O distance corresponding to a superoxide $(O_2)^{-1}$ grouping found in compounds such as KO_2 and CsO_2, is 1.3 Å [15]. If the ratio of the occupancy factors of O3 and O4 is two or less, then the formation of the short bond is not required and the excess oxygen O4 would be surrounded by two O3 at either 2.41 Å or 2.63 Å, and

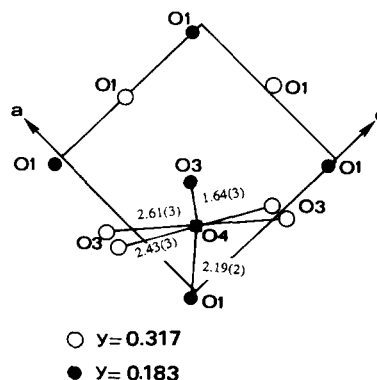Fig. 2. A projection of the section containing O1, O3, and O4 atoms (0.183 ≤ y ≤ 0.317) on the ac plane. The orthorhombic unit cell is outlined.

two O1 at 2.19 Å. The latter is a short O–O distance, but it is sometimes found in "normal" oxide compounds. The estimated standard deviation of the ratio $p_{O3}/p_{O4}=3.0$, is ± 0.4. Therefore, the model without the peroxide bond is within 2.5 times the standard deviation and cannot be excluded a priori. Nevertheless, the occupancy factor of the O3 can also be deduced from that of O1 (0.943(5)). Since the O1 and O3 occupancy factors were varied independently during the refinements, the value of $(1-0.943)=0.057$ represents an independent determination of the O3 occupancy factor. This strongly corroborates our model of O4 surrounded by three O3 and one O1 and the formation of the short O3–O4 bond.

The present structural study shows that each O4 atom forms an O$_2$ grouping with one O3. Since the formal valence of such grouping is taken as -2, the oxygen doping does not bring about any change in the formal cation valence. For every O4 that enters the structure as -1, one O3 decreases its valence from -2 to -1.

Figure 3 shows a projection of five unit cells of the La$_2$CuO$_{4.032}$ structure on the ac plane. Only La, O1, O3, and O4 are shown. The introduction of O4 has a double effect on the La coordination: on one hand it increases the coordination of the four first-nearest
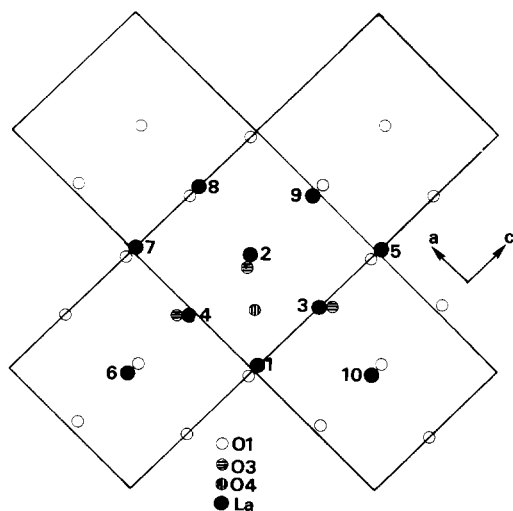
La neighbors (La$_{1-4}$ in fig. 3) and on the other it causes the variation of some of the nine La–O distances for ten La cations, namely the four first-nearest neighbors and six second-nearest ones (La$_{5-10}$ in the same figure). Depending upon the choice of the O3 position (from which it results either O3–O4 = 2.61 Å×2 or 2.43 Å×2, or 2.61 Å×1+2.43 Å×2) the modification of the environment of La$_1$, La$_2$, La$_7$, and La$_{10}$ is slightly different.

It is not too meaningful to discuss formal valences when the compound contains strong covalent bonds between anions as in the case of La$_2$CuO$_{4.032}$. However, qualitatively it can be stated that the increase of the coordination number of some of the La cations and the readjustment of the corresponding La–O distances, should correspond to a variation of the charge distribution. Formal valences can be calculated from the relationship between bond length and bond strength by using the formula and the constants given by Zachariasen [16]. For the La cations one obtains the value of 2.57 v.u. when the distortion due to O4 is not taken into account. This smaller value than the expected 3, is probably due to the empirical values of the constants. Zachariasen pointed out the anomalous behavior of lanthanum when compared to the other rare-earth cations. For example, if one calculates the valence of La in La$_2$O$_3$ in the A structure of sesquioxides, an unreasonable value is obtained. For this reason the structure of La$_2$O$_3$ was believed to be wrong for a long time. In our case the values of the constants are not important because we take into consideration a difference between two valences.

Table III lists the values of the valences for the ten La cations which are affected by the introduction of O4, together with the average La$_{1-10}$–O distances. It can be seen that the variation of the interatomic distances strongly indicate a readjustment of the electrostatic charges around the La cations. For four of them the valence increases, for four others it remains somewhat unchanged, while for two the valence decreases. This corresponds to an average total increase of 0.3 v.u. Since the Cu sublattice is only slightly affected by the introduction of O4, all the cation valence increase occurs on the La sublattice. When the structure of YBa$_2$Cu$_3$O$_7$ was determined in detail it was reasonable to attribute the extra charge to the Cu sublattice, but, as indicated layer by NMR,

Fig. 3. A projection on the ac plane of five orthorhombic unit cells. Only the La, O1, O3, O4 of half unit cell ($a \times b/2 \times c$) are represented.

Table III

	La–O(2.43×2)	v(La)(2.43×2)	La–O(2.61×2)	v(La)(2.61×2)
La1	2.69	2.92	2.73	2.76
La2	2.70	2.82	2.73	2.66
La3	2.64	3.03	2.64	3.03
La4	2.58	3.67	2.58	3.67
La5	2.58	3.28	2.58	3.28
La6	2.58	3.28	2.58	3.28
La7	2.69	2.48	2.65	2.64
La8	2.69	2.48	2.69	2.48
La9	2.74	2.25	2.74	2.25
La10	2.69	2.48	2.65	2.64
average	2.66	2.87	2.66	2.87

EXAFS, and XPS measurements, it actually corresponds to holes in the oxygen 2p band. In the present case as well the cation charge excess could be the result of holes in the same band.

The above discussion is valid only for a model where the distortion induced by a given O4 does not overlap with that induced by one of the adjacent O4. If these atoms are distributed isotropically in the structure, then one every eighth cell contains an O4 and the corresponding distortion. The average distance between two O4 is about $(8 \times 5.4 \times 13.2 \times 5.4)^{1/3} = 14.5$ Å. It would be a good approximation to assume that one O4 is contained in all cell whose volume is about $(2\sqrt{2}a \times b \times 2\sqrt{2}c)$. In this case there would exist columns of affected cells, running along the b axis and their distribution on the ac plane could be that of fig. 4. With such distribution the O4–O4 distance is about 14.5 Å. Note that there are not large O4-free areas.

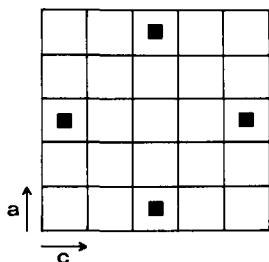As stated in the introduction Jorgensen et al. [8] have shown that at 320 K a phase separation occurs.

Fig. 4. One possible distribution of the unit cells containing O4 (indicated by black squares) on the ac plane.

From their data they argue that one phase is superconducting while the other is not. The powder pattern can only be indexed on two sets of lattice parameters: the a and b values are identical for the two sets while the two c values differ about $\frac{1}{5} \times (a-c)$. The single-crystal and the powder diffraction data could be reconciled if one assumes that the O4 atoms are in some way more clustered together than described above. For example, there could be one O4 per half cell ($a \times b/2 \times c$). The superconducting samples would be comprised of two types of domains, one with the O4 excess and the other without and these domains would be larger than the diffraction correlation length. For our single-crystal diffraction data collection we used a short neutron wavelength (0.48417 Å) in order to minimize the reflection splittings due to the difference between a and c, which allowed us to apply a twinning correction. Furthermore, the short wavelength reduced the effects of multiple diffraction. With such experimental conditions we could not possibly detect the phase separation, even if present in our sample. It is conceivable that the difficulties in locating the extra oxygen atoms at room temperature are not entirely due to large thermal vibrations for the oxygen atoms, but also to a somewhat incomplete phase separation which would increase with decreasing temperature. Neutron diffraction work on crystals exhibiting better Meissner effect than that of the present crystal, is in progress.

Very recent powder X-ray diffraction data taken with the high resolution powder diffractometer at beam line X13A at Brookhaven NSLS on $La_2CuO_{4+\delta}$,

have confirmed the phase separation detected by neutron diffraction [17].

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