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The Crystal Structure of Superconducting $\text{La}_2\text{CuO}_{4.032}$ by Neutron Diffraction

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Abstract

The structure of superconducting $\text{La}_2\text{CuO}_{4.032}$ has been determined by single-crystal neutron diffraction data. The excess oxygen, O4, is located between two adjacent LaO1 layers. The presence of O4 distorts the apical-oxygen O1 sublattice in such that each O4 forms a short bond (1.64 Å) with one O1, which indicates the formation of a strong covalent bond between these two atoms. The Cu and O2 sublattices as well as that of La are not affected by O4, however, 1.6% of the La cations increase their coordination from 9 to 10.

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 "undoped" 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 $\text{La}_2\text{CuO}_{4+\delta}$ 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).

Because of the uncertainties about the position and the bonding of the excess oxygen in superconducting $\text{La}_2\text{CuO}_{4+\delta}$ samples, we have carried out the crystal structure determination of a superconducting $\text{La}_2\text{CuO}_{4.032}$ single crystal by neutron diffraction data taken at room temperature and 15 K.

The crystal was grown in a CuO flux [4]. It was then treated at 500°C under oxygen pressure ($p_{\text{O}_2} = 3$ kbar) for 62 h and cooled slowly to room temperature.

The superconducting transition temperature for the single crystal was obtained by a.c. susceptibility measurements. The volume of the superconducting phase was estimated to be about 70% with an onset at 37.5 K (Fig. 1).

The neutron diffraction intensities were collected at room temperature and 15 K using the D-9 four-circle diffractometer at the ILL reactor ($\lambda = 0.48417$ Å). The intensities of ten of the strongest reflections were measured every 5 K on both side of the superconducting transition temperature. No measurable change, indicating a structural transition, was detected. The crystal was twinned but the systematic absences of the space group $Cmca$ allowed the determination of the percentage of each individual in the crystal (a value of 0.46 was obtained in the final refinement).

The refinement of the cation sites occupancy indicates that the La/Cu ratio is exactly 2 in this crystal. Since the cation

lattices do not compromise any vacancies, the structure must contain an excess oxygen. We chose to localize this oxygen excess from crystal chemical considerations (analogy to the structure of $\text{La}_2\text{NiO}_{4+\delta}$ [6]) and then try to refine its position ($1/4 y 1/4$). We used the low temperature data because in this case the thermal effects are minimized.

We found an excess oxygen O4 at $x = 1/4, y = 0.243, z = 1/4$ with a population $p_{\text{O4}} = 0.016(2)$. We found also that the site O3 at $x = 0.031(5), y = 0.182(2), z = 0.101(5)$ was occupied with a population $p_{\text{O3}} = 0.023(2) \times 2$. Since this position is just 0.75 Å from that of O1 (apical oxygen of the octahedron) it can only be occupied when O1 is empty. Therefore O3 should be interpreted as the result of displacements of some of the O1 anions. Very likely, the excess oxygen O4 is responsible for these displacements. 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 results based on the 15 K data after the final refinement are reported in Table I. The results based on the room temperature data were in agreement with the low temperature ones.

The structure of $\text{La}_2\text{CuO}_{4.032}$ is schematized in Fig. 2. 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 CuO_2 layers are separated from each other by two LaO1 layers. The excess oxygen O4 atoms are located between two LaO1 layers, at the center of cubes whose corners are occupied by four La and four O1 atoms. Each time that an O4 site is occupied, four La cations become ten coordinated, but their position is not affected. On the contrary, as stated above, this excess oxygen brings about the displacement of the O1 atoms toward the O3 sites. The list of all possible O1–O4, O3–O4 distances is: O1–O4 = $2.19(2)$ Å $\times 2$,

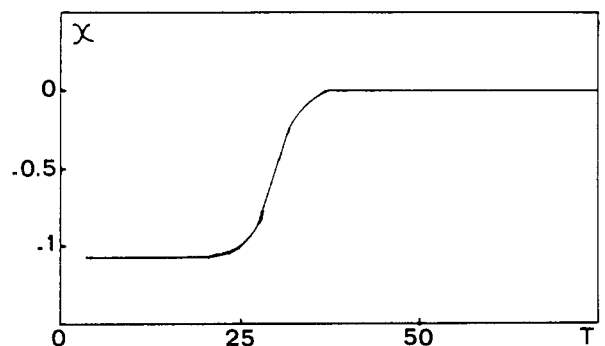


Fig. 1. a.c. Susceptibility of the $\text{La}_2\text{CuO}_{4.032}$ single crystal used for neutron diffraction.

Table I.

Refinement 15 K			
yLa	0.36111(4)	U La 11	0.0055(7)
zLa	0.0069(1)	U La 22	0.0030(2)
yO1	0.18307(8)	U La 33	0.0022(6)
zO1	-0.0356(3)	U La 23	0.0002(2)
yO2	-0.00697(7)	U Cu 11	0.0042(9)
xO3	0.030(5)	U Cu 22	0.0050(3)
yO3	0.182(2)	U Cu 33	-0.0001(8)
zO3	0.100(5)	U O1 11	0.0077(6)
yO4	0.243(4)	U O1 22	0.0040(3)
		U O1 33	0.0123(5)
		U O1 23	-0.0014(4)
nO1	0.943(5)	U O2 11	0.0055(7)
nO2	0.993(4)	U O2 22	0.0094(3)
nO3	0.024(2)	U O2 33	0.0023(6)
nO4	0.016(2)	U O2 13	0.0007(2)
$R_w(F^2)$	5.13%		
$R_{int}(F^2)$	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		
Cu-O4	3.72(4) × 4	O2-O2	2.6750(6) × 2
			2.7052(6) × 2
La-O1	2.352(1) × 1	O2-O3	2.76(3) × 2
	2.537(2) × 1		2.87(3) × 2
	2.7417(3) × 2		3.34(3) × 2
	2.986(2) × 1		3.47(3) × 2
La-O2	2.5923(8) × 2	O1-O4	2.19(2) × 2
	2.6812(8) × 2		2.02(2) × 2
La-O3	2.27(3) × 2	O3-O4	1.64(3) × 2
	2.64(3) × 2		2.43(3) × 2
	3.26(3) × 2		2.61(3) × 2
La-O4	2.36(3) × 2		1.89(3) × 2
	2.43(3) × 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 (O₂)⁻² peroxide grouping. The values found in peroxide compounds such as BaO₂ is about 1.5 Å [7], whereas the O-O distance corresponding to a superoxide (O₂)⁻¹ grouping found in compounds such as KO₂ and CsO₂, is 1.3 Å [8].

The present structural study shows that each O4 atom forms an O₂ grouping with one O3. Since the formal valence of such grouping is taken at -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.

Fig. 3 shows a projection of five unit cells of the La₂CuO_{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 neighbours (La₁₋₄ 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

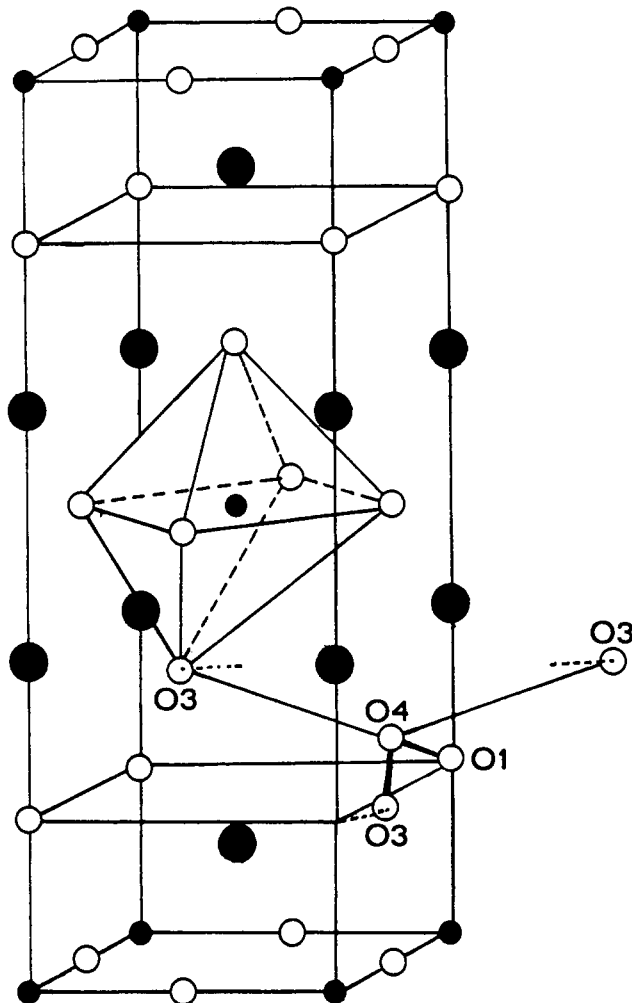


Fig. 2. The position of O4 in the pseudo tetragonal unit cell of La₂CuO_{4.032}. The displaced O4 atoms to the O3 positions are indicated.

nearest neighbours and six second-nearest ones (La₅₋₁₀ in the same figure).

It is not too meaningful to discuss formal valences when the compound contains strong covalent bonds between

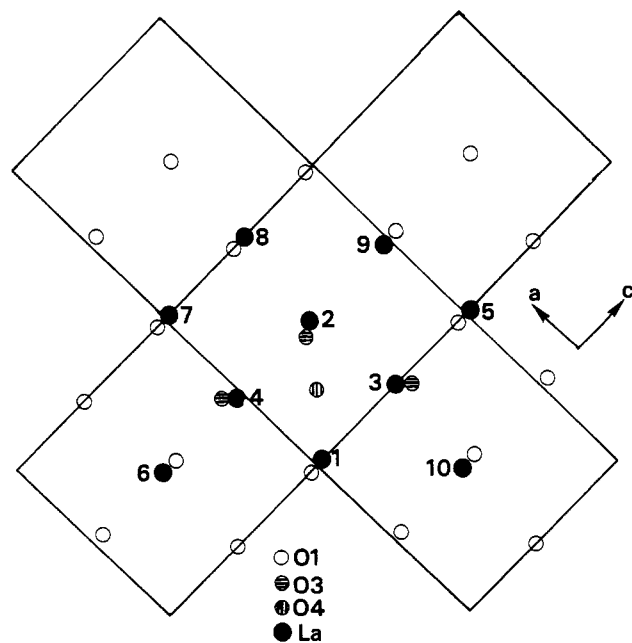


Fig. 3. A projection on the a.c. plane of five orthorhombic unit cells. Only the La, O1, O3, O4 of half unit cell ($a \times b/2 \times c$) are represented.

anions as in the case of $\text{La}_2\text{CuO}_{4.032}$. 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 readjustment of the electrostatic charges around the La cations. La valence calculations using the Zachariasen formula indicate 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 $\text{YBa}_2\text{Cu}_3\text{O}_7$ was determined in detail it was reasonable to attribute the extra charge to the Cu sublattice, but, as indicated later by NMR, 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. Consequently, there are not large O4-free areas.

Jorgensen *et al.* [9] have shown that at 320 K a phase separation occurs. 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 of about $1/5 \times (a-c)$. 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. The superconducting samples would be composed 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.

Because of our experimental conditions (short wavelength) we could not possibly detect the phase separation, even if present in our sample. Neutron diffraction work on crystals exhibiting better Meissner effect than that of the present crystal, and using a longer wavelength is in progress.

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