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

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Abstract

The structure of superconducting La$_2$CuO$_{4.032}$ has been determined by single-crystal neutron diffraction data. The excess oxygen, O$_4$, is located between two adjacent LaO$_1$ layers. The presence of O$_4$ distorts the apical-oxygen O$_1$ sublattice in such that each O$_4$ forms a short bond (1.64 Å) with one O$_1$, which indicates the formation of a strong covalent bond between these two atoms. The Cu and O$_2$ sublattices as well as that of La are not affected by this excess from crystal chemical considerations (analogy to the structure of La$_2$NiO$_{4.4}$[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 O$_4$ at $x = 1/4$, $y = 0.243$, $z = 1/4$ with a population $p_{O4} = 0.016(2)$. We found also that the site O$_3$ at $x = 0.031(5)$, $y = 0.182(2)$, $z = 0.101(5)$ was occupied with a population $p_{O3} = 0.023(2) \times 2$. Since this position is just 0.75 Å from that of O$_1$ (apical oxygen of the octahedron) it can only be occupied when O$_1$ is empty. Therefore O$_3$ should be interpreted as the result of displacements of some of the O$_1$ anions. Very likely, the excess oxygen O$_4$ is responsible for these displacements. From the ratio of the occupancy factors of O$_3$ and O$_4$, it can be deduced that for each O$_4$ three O$_1$ are displaced to O$_3$.

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 La$_2$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 LaO$_1$ layers. The excess oxygen O$_4$ atoms are located between two LaO$_1$ layers, at the center of cubes whose corners are occupied by four La and four O$_1$ atoms. Each time that an O$_4$ 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 O$_1$ atoms toward the O$_3$ sites. The list of all possible O$_1$–O$_4$, O$_3$–O$_4$ distances is: O$_1$–O$_4$ = 2.19(2) Å × 2,

![Fig. 1. a.c. Susceptibility of the La$_2$CuO$_{4.032}$ single crystal used for neutron diffraction.](image-url)
Table I.

Refinement 15 K

|  |  |  |  |
|---|---|---|---|
| $y_{La}$ | 0.3611(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) |
| $n_{O1}$ | 0.943(5) | U | O2 22 | 0.0123(5) |
| $n_{O2}$ | 0.993(4) | U | O2 33 | -0.0014(4) |
| $n_{O3}$ | 0.024(2) | U | O2 22 | 0.0023(6) |
| $n_{O4}$ | 0.016(2) | U | O2 13 | 0.0007(2) |
| $R_p(F^2)$ | 5.13% |  |  |  |
| $R_w(F^2)$ | 3.88% |  |  |  |
| $\chi^2$ | 4.20 |  |  |  |

Interatomic Distances

|  |  |  |  |
|---|---|---|---|
| Cu-O1 | 2.415(1) x 2 | O1-O2 | 3.061(1) x 2 |
| Cu-O2 | 1.9022 x 4 | O2-O2 | 2.6750(6) x 2 |
| Cu-O3 | 2.46(2) x 2 |  | 2.7052(6) x 2 |
| Cu-O4 | 3.72(4) x 4 | O2-O3 | 2.76(3) x 2 |
| La-O1 | 2.3521(1) x 1 | O2-O3 | 2.87(3) x 2 |
|  | 2.537(2) x 1 |  | 3.34(3) x 2 |
|  | 2.7417(3) x 2 |  | 3.47(3) x 2 |
|  | 2.986(2) x 1 |  |  |
| La-O2 | 2.5923(8) x 2 | O1-O4 | 1.64(3) x 2 |
|  | 2.6812(8) x 2 |  | 2.43(3) x 2 |
| La-O3 | 2.27(3) x 2 | O3-O4 | 2.61(3) x 2 |
|  | 2.64(3) x 2 |  |  |
|  | 3.26(3) x 2 |  |  |
| La-O4 | 2.36(3) x 2 |  | 1.89(3) x 2 |
|  | 2.43(3) x 2 |  |  |

Fig. 2. The position of O4 in the pseudo tetragonal unit cell of La$_2$CuO$_{4+4}$. The displaced O4 atoms to the O3 positions are indicated.

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 x h/2 x c) are represented.

2.02(2)Å x 2, O1-O3 = 1.64(3)Å x 2, 1.89(3)Å x 2, 2.43(3)Å x 2, 2.61(3)Å x 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 x 2, or O4-O1 = 2.19 Å and O4-O3 = 2.43 Å x 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 [7], 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 [8].

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 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 La$_2$CuO$_{4+4}$ 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 (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 neighbours and six second-nearest ones (La$_{5-16}$ in the same figure).

It is not too meaningful to discuss formal valences when the compound contains strong covalent bonds between
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anions as in the case of La$_4$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 YBa$_2$Cu$_3$O$_6$ 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 $(a-c)$. 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 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. 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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