Hexagonal doping pattern in high temperature superconducting La$_2$CuO$_{4+\delta}$ formed by regular triangles

H.P. Roeser$^a,$*, F. Hetfleisch$^a,$ D.T. Haslam$^a,$ J.S. López$^a,$ M. Stepper$^a,$ J. Vernerey$^a,$ F.M. Huber$^b,$ M.F. von Schoenermark$^a,$ A.S. Nikoghosyan$^c$

$^a$Institute of Space Systems, Universität Stuttgart, Pfaffenwaldring 31, 70569 Stuttgart, Germany
$^b$German Aerospace Center, GSGC, Muenchnerstr. 20, 82234 Wessling, Germany
$^c$Department of Microwave and Telecommunication, Yerevan State University, Alex Manoogian 1, Yerevan 375025, Armenia

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1. Introduction

High temperature superconductors (HTSC) which have tetragonal or orthorhombic (with lattice constant $a \approx b$) structures and only one doping position within a unit cell, can only form homogeneous doping patterns built up by squares. For these HTSCs, the doping distance $x$ projected on the superconducting CuO$_2$ plane is given by

$$x^2 = (z_i^2 + z_j^2) \cdot a^2$$

with $z_i, z_j \in \mathbb{N}$. Examples are hole-doped YBa$_2$Cu$_3$O$_7$ (Y123) with one ($n = 1$) superconducting CuO$_2$ plane, La$_{2-x}$Ca$_x$CuO$_4$ (LCCO) and Bi-2212 with $n = 2$, Bi-2223 with $n = 3$ and electron-doped Pr$_{1-\delta}$LaCe$_\delta$CuO$_{4-\delta}$ (PLCCO) with a T'-structure and $n = 1$ [1–4].

The compound La$_2$CuO$_4$ is an anti-ferromagnetic insulator and becomes superconducting with a transition temperature $T_c$ up to $\sim 40$ K by partially replacing La-atoms by an alkaline earth or an alkali metal or by introducing interstitial oxygen. It is one of the best known HTSCs and it has a simple crystal structure, which has been investigated at 300 K and $T < T_c$ by different experimental methods like neutron diffraction, X-ray photoemission spectroscopy and X-ray powder diffraction [5–7]. The unit cell at 300 K contains two chemical formulas $2 \cdot [La_2CuO_4]$ and the stoichiometric compound La$_2$CuO$_4$ has the space group symmetry $Bmab$ with a tetragonal structure and lattice constant $a$ (Figs. 1 and 2).

$\ast$ Corresponding author. Tel.: +49 711 685 62375; fax: +49 711 685 63596. E-mail address: roeser@irs.uni-stuttgart.de (H.P. Roeser).
Fig. 1. The tetragonal crystal structure at \( T = 300 \text{ K} \) (left) is transformed into an orthorhombic structure (right) when cooled down to low temperatures. The different planes are numbered 1–11.

When introducing interstitial oxygen with an excess value up to \( \delta = 0.12 \) and cooling down to low temperatures \((T < T_c)\) a phase transition into a space group symmetry \( Fmmm \) occurs \([6,8]\) with lattice parameters \( a^* = 0.5354 \text{ nm}, b^* = 0.5384 \text{ nm} \) and \( c^* = 1.321 \text{ nm} \) which results in a maximum \( T_c \) at \( \delta = 0.08 \) \([7]\). Figs. 1 and 2 illustrate the phase transition and the cross sections of both unit cells. For the orthorhombic structure we have \( a^* = \sqrt{2} \cdot a \) and it contains 2 \([\text{CuO}_2]\) elements per unit cell cross section in the superconducting \( \text{CuO}_2 \) plane (e.g. plane number 6). The interstitial O-atoms are located on the symmetric axis in \( c \)-direction between adjacent LaO layers 2/3 and 4/5 as well as 7/8 and 9/10 \([6,7]\). Projecting the excess O-atom into the \( \text{CuO}_2 \) plane, from above or below, the excess atom can be placed above a Cu-atom or in the empty space between four O-atoms as illustrated in Fig. 3. The two configurations can be transformed into one another by shifting 0.5a on the ordinate and 0.5a on the abscissa. This is caused by the alternate displacement of the stacking sequence for \( \text{CuO}_2 \) planes. Both excess O-atom positions are equal (Fig. 3).

Now it is possible to form hexagonal doping patterns made up by regular triangles to obtain a closed packed homogeneous doping distribution in addition to the square distribution as illustrated in Figs. 3–6.
3. Hexagonal doping distribution by regular triangles

Fig. 3 illustrates a cut through a CuO$_2$ plane of an orthorhombic crystal structure. For simplicity it is assumed that $a^* \approx b^*$ which is the case for many HTSCs of this type. As shown in Figs. 1 and 2 the cross section of a unit cell consists of 2 \([\text{CuO}_2] \) elements so that an excess oxygen doping atom could “serve” two Cu-atoms and therefore be placed at two different positions when projected into the cross section of a unit cell. This is essential for a hexagonal doping structure formed by regular triangles, because to form a hexagonal structure by 2 \([\text{CuO}_2] \) elements it is necessary to divide the orthorhombic unit area into two parts with 1 \([\text{CuO}_2] \) element each. Fig. 4 shows the orthorhombic cross sections with 2 \([\text{CuO}_2] \) elements which can be split by both diagonals as well as both mid-vertices into two single \([\text{CuO}_2] \) elements.

In the following we will describe the special case of a planar hexagonal doping structure with regular triangles built up by nearly quadratic elements with $a \approx b$ in a more general form.

A regular hexagonal system is characterized by equilateral triangles and the ratio between side length $x$ to the height $h$ of the triangle is $h/x = \sqrt{3}/4 = 0.86603$. A hexagonal geometry of an orthorhombic crystal structure with $45^\circ$ between the tetragonal and orthorhombic lines (Fig. 6) can be described by eight equations:

$$x = z_1 \cdot a$$  
$$h = z_2 \cdot b/2 = z_1 \cdot a \cdot \sqrt{3}/4 = z_1 \cdot a \cdot 0.86603$$  
$$x^2 = 2 \cdot z_3^2 \cdot (d/2)^2$$  
$$z_4 = z_3 + z_5$$  

Fig. 3. A cut through the CuO$_2$ plane of orthorhombic unit cells shows two different possibilities for the position of oxygen excess atoms. The positions are arbitrarily chosen forming a square distribution described by $z_{10} = 9, z_{11} = 3, z_{12} = 6$ and $z_{13} = 3$.

Fig. 4. For both oxygen excess doping positions the unit cell can be divided by the diagonals as well as the mid-vertices into two CuO$_2$ elements and each time 1/2 oxygen excess atom is connected to 1 \([\text{CuO}_2] \) element.

$$z_3 = z_1$$  
$$x^2 = z_2^2 \cdot (d/2)^2 + (z_3 + z_5)^2 \cdot (d/2)^2$$  
$$h = [2 \cdot z_2^2 \cdot (d/2)^2]^{1/2} + [z_3^2 \cdot (d/2)^2 - z_5^2 \cdot (a/2)^2]^{1/2}$$  
$$F_o = 2 \cdot F_4 = x \cdot h = x^2 \cdot \sqrt{3}/4$$  

where $z_i \in \mathbb{N}$, $d^2 = a^2 + b^2$, $a \approx b$, $a < b$ and $b$ has been derived from $b^* = \sqrt{2} \cdot b$. $F_o$ is the rhombic area representing the superconducting unit area with one doping element as the sum of the contributions at the four corners, as shown in the next section. The value $x$ is assumed to be the doping distance. Eq. (9) also shows that a hexagonal doping structure is more compact than a square doping structure by a factor $\sqrt{3}/4$. Combining Eqs. (3), (6) and (8) we achieve

$$z_5 \cdot (d/2) \cdot \sqrt{3}/4 = z_1 \cdot [a \cdot \sqrt{3}/4 - b/2]$$

If $a \approx b$, the ratio of the two integers is given by

$$z_5/z_1 \approx \sqrt{3}/4 - 1/2 = 0.336 \quad \text{or} \quad z_5/z_1 \approx 2.7322$$

The highest closed packed doping density is given for the minimum of the rhombic area $F_o$ by choosing the smallest integers $z_1$ and $z_5$ and satisfying Eq. (11). These are $z_5 = 4$ and $z_1 = 11$ with $4/11 = 0.364$ and the other values for $z_1$ follow to $z_2 = 19$, $z_3 = 11$ and $z_4 = 15$ as shown in the following. Another combination of integers is $7/19 = 0.368$, representing the second smallest hexagon. But in this case the hexagonal area is $(7/4)^2 \approx 3$ times larger.

The doping density can be determined by using the same nomenclature for this compound as it has already been introduced by the authors [1–4] for different materials.
Fig. 5. Different doping density distributions for La$_2$CuO$_{4+x}$ with the same doping distance $x = 4.165$ nm in the CuO$_2$ plane: (a) square distribution, (c) hexagonal with regular triangles and (b) combination of (a) and (b).

Fig. 6. Superconducting CuO$_2$ plane of La$_2$CuO$_{4.08}$ (LCO). The distance between unit cells with oxygen excess atoms is the superconducting resonance length $x = 11 \cdot a = 4.165$ nm. The superconducting unit cell has the size of $A_{\text{SC}} \approx 105 \cdot$ CuO$_2$ unit cells resulting in a density of $\sim 2\%$. The oxygen excess contribution is given by $\delta$ and its density by $(\Sigma)^{-1}$. For a square doping pattern the superconducting unit area per doping atom within one CuO$_2$ plane is given by $(x_{\text{sq}})^2 = \Sigma \cdot (a^*)^2$, but for a hexagonal doping pattern the unit area is $A_{\text{SC}} = F_D = \sqrt{(3/4) \cdot \Sigma} \cdot (a^*)^2$ with $\Sigma = (z_4^2 + z_5^2)$). Therefore the hexagonal doping distance is given by $x = (\sqrt{(3/4) \cdot \Sigma})^{1/2} \cdot$ lattice constant $a^*$. By using Eq. (9) this leads to

$$x^2 = \sqrt{(4/3) \cdot F_D} = \sqrt{(4/3) \cdot \Sigma} \cdot a^2 = z_1^2 \cdot a^2 \quad (12)$$

Assuming $a \approx b$ we have

$$x^2 = z_1^2 \cdot a^2 \approx \sqrt{(4/3) \cdot 2 \cdot \Sigma} \cdot a^2 \approx 2.31 \cdot \Sigma \quad (13)$$

The hexagonal doping distance can also be determined using Pythagoras equations as illustrated in Fig. 6

$$(z_4^2 + z_5^2) \cdot (d/2)^2 \approx (z_3^2 + z_1^2) \cdot (d/2)^2 \approx z_1^2 \cdot a^2 \quad (14)$$

Assuming $a \approx b$ this leads to

$$(z_4^2 + z_5^2) \approx 2 \cdot z_1^2 \rightarrow 15^2 + 4^2 \approx 2 \cdot 11^2 \rightarrow 241 \approx 242 \quad (15)$$

and confirms the previous numbers. The deviation is only $241/242 = 0.996 \equiv 0.4\%$ which is compensated by $a^*/b^* = 0.994 \equiv 0.6\%$. For the smallest rhombic area $F_D$ the analysis provides $z_1 = 11$, so that the doping is given by Eq. (13) to $\Sigma = 52.4$ and $(\Sigma)^{-1} \equiv 1.91\%$. According to Eq. (9) the superconducting unit area $A_{\text{SC}}$ covers
A hexagonal doping structure with regular triangles can only be achieved for doping levels of \( \delta = 0.026 \) and \( \delta = 0.078 \). For other density levels between 0.02 < \( \delta < 0.09 \) a square doping distribution has to be chosen. According to Fig. 3 the doping distance \( x_{sq} \) can be determined by the following equation:

\[
(x_{sq})^2 = \frac{z_1}{10} + (z_1^2 - 1) \cdot \left( \frac{a/2}{\sqrt{3}} \right)^2 = \left( x_{12}^2 + x_{13}^2 \right) \cdot \left( \frac{a/2}{\sqrt{3}} \right)^2 = \Sigma a^2
\]

and the doping density \( \Sigma^{-1} \) is always connected to the actual unit cell size so that

\[
\Sigma = 1/4 \cdot (x_{12}^2 + x_{13}^2)
\]

with

\[
\Sigma^{-1} = \left( 1 - 4.00/(4.00 + \delta) \right) = \delta/(4 + \delta)
\]

The highest doping density with a hexagonal distribution \( \delta = 0.078 \approx 0.08 \) leads to a distance \( x = 11 \cdot a \). The same distance can be achieved also by a square distribution but at a lower doping density.

If \( x_{sq} = 11 \cdot a \rightarrow (x_{sq})^2/(\sigma^2) = 60.5 \rightarrow (x_{12}^2 + x_{13}^2) = 242 \approx 15^2 + 4^2 = 241 \). This leads to \( \Sigma = (4+\delta)/\delta = 60.5 \rightarrow \delta = 0.0117.8 \) and \( \Sigma^{-1} = 1.65 \).

It is worth noticing that in the interval 0.06 < \( \delta < 0.078 \) many combinations of square plus regular triangles distributions are possible by increasing or decreasing the number of strips with regular triangles as illustrated in Fig. 5 as one example.

### 5. Superconducting La\textsubscript{2}CuO\textsubscript{4+δ} (LCO)

In one chemical formula [La\textsubscript{2}CuO\textsubscript{4}] four O-atoms (4O\textsuperscript{2−}) need a total of eight electrons which are provided by 2La\textsuperscript{3+} + 1Cu\textsuperscript{2+}. This material has no Cu\textsuperscript{3+} elements and is not superconducting unless it is doped by an appropriate oxygen excess level. A small amount of interstitial oxygen between the copper–oxygen planes is responsible for the occurrence of superconductivity. At low temperatures the orthorhombic unit cell consists of \( 4 \cdot [\text{La}_2\text{CuO}_{4+\delta}] \) as illustrated in Fig. 1. This means that one unit cell can accommodate two O-atoms where each O-atom connects with two chemical formulas \( 2 \cdot [\text{La}_2\text{CuO}_{4+\delta}] \) forming a chemical arrangement of \( 4\text{La}^{3+} + 2\text{Cu}^{3+} + 9\text{O}^2− \). The cross section of the superconducting unit cell consists of \( 2 \cdot [\text{CuO}_2] \) elements and one excess O-atom transforms \( 2\text{Cu}^2+ \) into \( 2\text{Cu}^3+ \)-ions. Only half an O-atom per chemical formula is necessary. Therefore, we only need half O-atom per chemical formula with the consequence that the density of half oxygen excess atoms has to be calculated by using the value \( 2 \cdot \delta \). On the other hand \( \text{La}_2\text{CuO}_4 \) comes as pairs in the orthorhombic unit cell with the consequence that a value of \( 2 \cdot \delta/2 = \delta \) should be used to calculate the oxygen doping distance.

The superconductivity of \( \text{La}_2\text{CuO}_4+\delta \) has been intensively investigated for doping levels \( 0 < \delta < 0.13 \). Two orthorhombic phases can be distinguished by means of X-ray data: a metallic superconducting oxygen-rich phase for \( \delta > 0.06 \) and a second phase for \( \delta < 0.06 \) which leads to an insulating anti-ferromagnetic oxygen-poor phase at \( \delta < 0.01 \). It has also been found that in the doping range \( 0.06 < \delta < 0.09 \) the transition temperature has its maximum. In this orthorhombic phase the interstitial O-atoms form an ordered system throughout the crystal which means that they are homogeneously distributed. Also, Seebeck data indicate a nearly constant concentration of itinerant holes in the superconducting CuO\textsubscript{2} planes. The highest transition temperature \( T_c \) for LCO has been achieved for an O-atom excess level of \( \delta = 0.08 \) leading to onset temperatures of \( T_c \) of 40 K and a middle \( T_c = 40 \pm 1.5 \) K which is considered to be taken at half the transition interval of the resistivity temperature curves. This interstitial oxygen level leads to a density of \( \Sigma^{-1} = (1-4.00/4.08) = 1.961 \cdot 10^{-2} \equiv 1.96 \% \) and \( \Sigma = 51.0 \). If we assume that a hexagonal distribution with regular triangles is the choice than the doping distance \( x \) can be calculated according to Eq. (13) to \( x^2 + a^2 = \Sigma^2 \cdot 2.31 \cdot a^2 \) with \( z_1 = 10.9 \approx 11 \) because this is the next closest integer. Therefore, the doping distance \( x \) results in \( x = 11 \cdot a = 11 \cdot 0.3786 \text{nm} = 4.165 \text{nm} \) (Fig. 6).

### Table 1

<table>
<thead>
<tr>
<th>Material</th>
<th>( T_c ) (K) exp.</th>
<th>Crystal structure at ( T &lt; T_c ) with doping (nm)</th>
<th>Excess oxygen doping distance ( \delta )</th>
<th>( \Sigma^{-1} ) (%)</th>
<th>( x ) (nm)</th>
<th>( (2x)^2 \cdot 10^{-15} ) (m(^2))</th>
<th>( T_c ) (K) calc.</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{La}<em>2\text{CuO}</em>{4+\delta}, \text{LCO} )</td>
<td>40 ± 1.5</td>
<td>( \alpha^* = 0.5354 ), ( \beta^* = 0.5384 ), ( c^* = 1.321 )</td>
<td>0.08 &lt; 2.0</td>
<td>4.165</td>
<td>69.4</td>
<td>40.0</td>
<td>40.0</td>
</tr>
</tbody>
</table>
unit cells, has a density given by \( \delta = 0.078 \) and a doping distance of \( x = 11 \cdot a \). The variation of \( T_c \) in the doping range \( 0.065 < \delta < 0.085 \) is very flat and \( T_c \) is not significantly smaller at both ends of the \( \delta \) range compared to \( T_c \) at \( \delta = 0.08 \) [10]. But in Section 4 it has been shown that square and hexagonal doping patterns in combination might also be possible with the same doping distance \( x \). This means that independent of the doping level in the range \( 0.067 < \delta < 0.078 \) the doping distance \( x \) could be the same. The consequence is that \( T_c \) stays the same according to Eq. (1) and the experimental \( T_c = 40 \pm 1.5 \) K compares very well with the calculated \( T_c = 40 \) K (Table 1).

It is interesting to note that in 1993 the existence of a large superstructure with an extension in the order of 10 times the unit cell—compared to \( x = 11 \cdot a \) in this paper—has been reported, which suggests that ordering patterns span many fundamental unit cells [6].

References


