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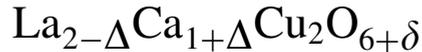
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ACADEMY TRANSACTIONS NOTE

Doping structure of the high temperature superconductor



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**Abstract**

The double doped unit cell of  $\text{La}_{2-\Delta}\text{Ca}_{1+\Delta}\text{Cu}_2\text{O}_{6+\delta}$  (LCCO-52) consists of two chemical formulas,  $\text{La}_2\text{CaCu}_2\text{O}_7$  and  $\text{Ca}_3\text{Cu}_2\text{O}_6$  which are responsible for the occurrence of superconductivity with  $n = 2$  superconducting  $\text{CuO}_2$  planes per chemical formula. The distance  $x$  between double doped unit cells projected into a  $\text{CuO}_2$  plane matches the experimental transition temperature  $T_c$  quite well.

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**1. Introduction**

The ternary compound  $\text{La}_2\text{CuO}_4$  is the parent material for several high temperature superconductors (HTSC) by doping with an alkaline earth or alkali metal (Ba, Sr, Ca, Na, K, ...) and/or introduction of oxygen deficiency or interstitial oxygen excess within the crystal. Multi-layered  $\text{CuO}_2$  planes per chemical formula ( $n > 1$ ) offer even higher critical transition temperatures  $T_c$  than single  $\text{CuO}_2$ -layer cuprates. Although this family of cuprates has been the subject of an extraordinary research effort in the last 20 years, it is still unclear why some materials with different chemical compositions are HTSCs and others are not.

One reason for the mystery might come from the fact that the simple tetragonal crystal structure at room temperature is changing at low temperatures for most of these HTSCs into an orthorhombic crystal structure, which is caused by a rotation/tilting of the Cu-atom centered oxygen octahedron [1,2].

In this paper we will analyze the crystal structure of the double-doped  $\text{La}_{2-\Delta}\text{Ca}_{1+\Delta}\text{Cu}_2\text{O}_{6+\delta}$  material and tie it to the correlation shown in Eq. (1) between the doping structure value  $(2x)^2$  and  $T_c$  as detailed in prior publications [3–6].

$$(2x)^2 \cdot n^{-2/3} \cdot 2M_{\text{eff}} \cdot \pi k T_c = h^2 \tag{1}$$

**2. Crystal structure of  $\text{La}_{2-\Delta}\text{Ca}_{1+\Delta}\text{Cu}_2\text{O}_{6+\delta}$  (LCCO-52)**

The 2126 two- $\text{CuO}_2$ -layer compound ( $n = 2$ ) is doped with Ca-atoms and also with oxygen excess.

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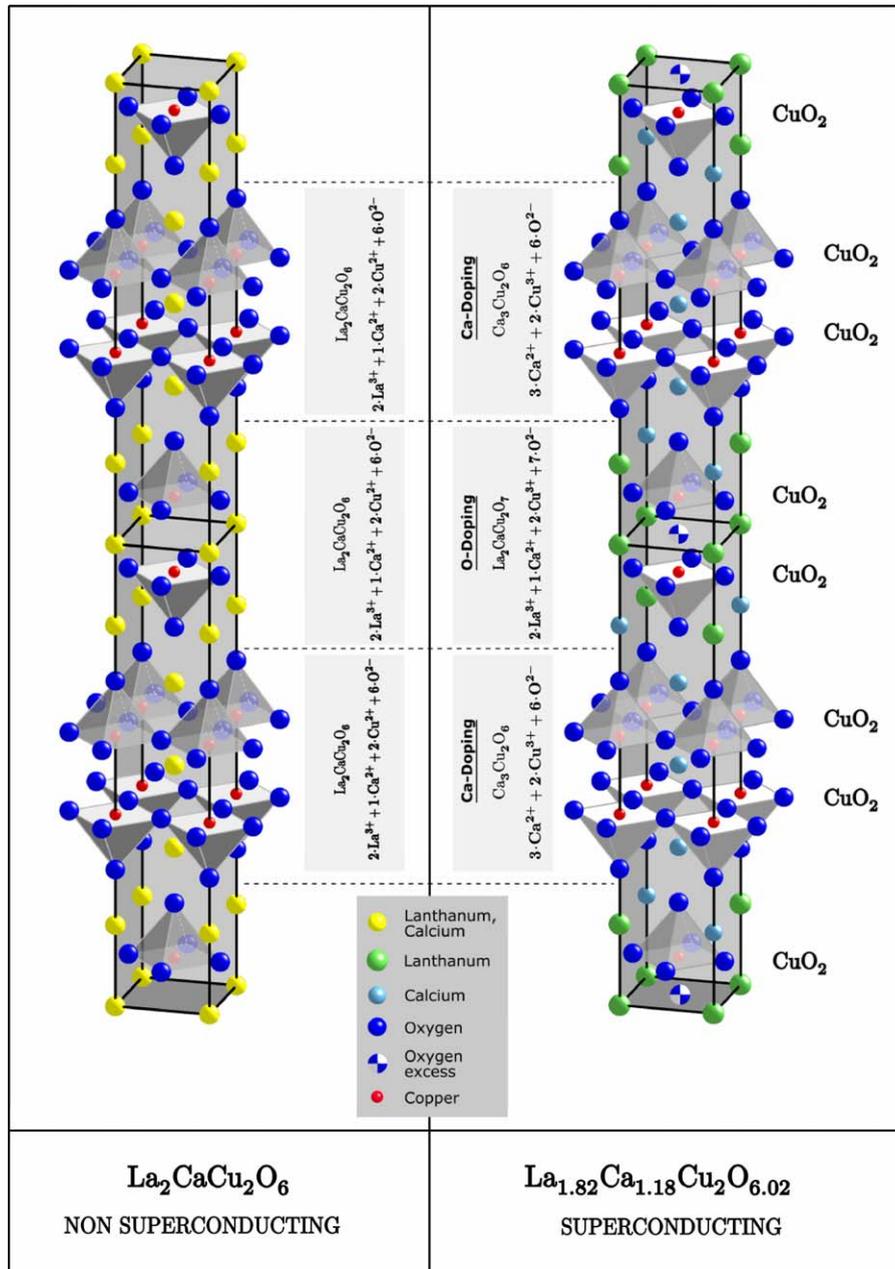


Fig. 1. Crystal structure and electronic arrangement of non-superconducting and superconducting  $\text{La}_{2-\Delta}\text{Ca}_{1+\Delta}\text{Cu}_2\text{O}_{6+\delta}$ .

This material is a very well studied HTSC with an onset temperature starting at  $T_c$  (onset)  $\approx 60\text{K}$  [7,8]. It has a simple tetragonal crystal structure (Fig. 1) and the unit cell ( $a = 0.383\text{ nm}$ ,  $c = 1.945\text{ nm}$ ) consists of  $2 \cdot [\text{La}_{2-\Delta}\text{Ca}_{1+\Delta}\text{Cu}_2\text{O}_{6+\delta}]$ . This HTSC does not change its crystal structure when cooling down to low temperatures [9,10]. Ca-atom doping keeps the tetragonal crystal structure because the ionic radius of  $\text{Ca}^{2+}$

(0.099 nm) is smaller than for  $\text{La}^{3+}$  (0.106 nm) and  $\text{Sr}^{2+}$  (0.112 nm). Fig. 1a illustrates the crystal structure for the undoped material  $\text{La}_2\text{CaCu}_2\text{O}_6$ . In one chemical formula  $[\text{La}_2\text{CaCu}_2\text{O}_6]$  six O-atoms ( $6\text{O}^{2-}$ ) need 12 electrons which are provided by  $2\text{La}^{3+} + 1\text{Ca}^{2+} + 2\text{Cu}^{2+}$ . This material has no  $\text{Cu}^{3+}$ -element and is not superconducting unless  $\text{La}^{3+}$  is substituted by  $\text{Ca}^{2+}$  and the material is doped by an appropriate oxygen excess

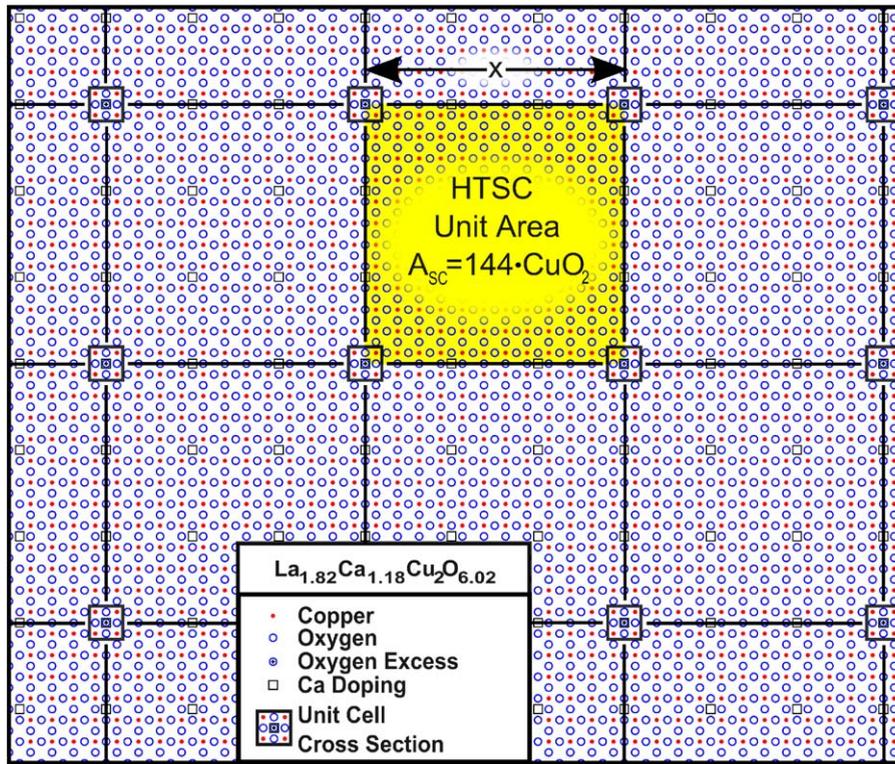


Fig. 2. Superconducting  $\text{CuO}_2$  plane of  $\text{La}_{1.82}\text{Ca}_{1.18}\text{Cu}_2\text{O}_{6.02}$  (LCCO-52) with a T-crystal structure ( $a = b = 0.383 \text{ nm}$ ). The distance between double doped unit cells is the superconducting resonance length  $x = 4.60 \text{ nm}$ . The superconducting unit area has the size of  $144 \cdot \text{CuO}_2$  unit areas.

level at the same time. A small amount of interstitial oxygen in the middle of the unit cell in combination with an optimized Ca-atom doping is responsible for the occurrence of superconductivity.

The superconducting compound has been investigated by neutron diffraction and scattering measurements [9–11]. The data shows the following:

- (a) Oxygen excess is intercalated between two  $\text{CuO}_2$  planes and the extra O-atom forms a cluster with  $\text{La}^{3+}$ -ions at that position
- (b)  $\text{Ca}^{2+}$ -ions show a strong preference for positions in between oxygen excess layers.

The atomic composition of the double doped unit cell is illustrated in Fig. 1b with the following electronic arrangements:

- (a)  $2\text{La}^{3+} + 1\text{Ca}^{2+} + 2\text{Cu}^{3+} + 7\text{O}^{2-}$  for the oxygen excess position bridging two  $\text{CuO}_2$  planes originally containing  $\text{Cu}^{2+}$ -ions. The introduction of an extra O-atom between the two  $\text{CuO}_2$  planes takes one extra electron from above and one from below.

Therefore, we only need half an O-atom per  $\text{CuO}_2$  plane with the consequence that the density of half oxygen excess atoms has to be calculated by using the value  $2 \cdot \delta$ .

- (b)  $3\text{Ca}^{2+} + 2\text{Cu}^{3+} + 6\text{O}^{2-}$  for the Ca-doped positions. In this chemical formula there are no La-atoms. This has the consequence that the doping density of  $\Delta$  in  $\text{La}_{2-\Delta}\text{Ca}_{1+\Delta}\text{Cu}_2\text{O}_{6+\delta}$  has to be related to three atoms instead of two.

Obviously the unit cell consists of two different chemical formulas and creates four superconducting highways ( $4 \cdot \text{CuO}_2$  planes doped with  $\text{Cu}^{3+}$  ion positions) per unit cell.

The idea of considering different chemical formulas in one unit cell has already been suggested for  $\text{La}_{2-\Delta}\text{Sr}_\Delta\text{CaCu}_2\text{O}_{6+\delta}$  by Ulrich et al. [12].

### 3. Optimum doping of $\text{La}_{2-\Delta}\text{Ca}_{1+\Delta}\text{Cu}_2\text{O}_{6+\delta}$

The double doping concept has already been introduced by the authors [4–6], and we will use the same nomenclature for this compound. The oxygen

Table 1

Structural data of superconducting  $\text{La}_{1.82}\text{Ca}_{1.18}\text{Cu}_2\text{O}_{6.02}$  and comparison between the experimental and calculated transition temperature  $T_c$ .

Material	$T_c$ exp. (K)	Crystal structure (nm)	Excess oxygen distance			Atomic doping			Carrier distance $x_3$ (nm)	$(2x_3)^2 \cdot n^{-2/3} \times 10^{-18}$ ( $\text{m}^2$ )	$T_c$ calc. (K)
			$\delta$	$(\Sigma_1)^{-1}$ (%)	$x_1$ (nm)	$\Delta$	$(\Sigma_2)^{-1}$ (%)	$x_2$ (nm)			
$\text{La}_{2-\Delta}\text{Ca}_{1+\Delta}\text{Cu}_2\text{O}_{6+\delta}$ LCCO-52	$52.4 \pm 1$	$a = 0.383,$ $c = 1.945$	0.02	0.7	4.60	0.18	6.25	1.53	4.60	$53.23 \cdot n = 2$	52.2
									$A_{sc} = 144 \cdot \text{CuO}_2$		

deficiency contribution is given by  $\delta$ , its density by  $(\Sigma_1)^{-1}$ , the number of unit areas per doping atom within one  $\text{CuO}_2$  plane by  $\Sigma_1 = (z_1^2 + z_2^2)$  and the doping distance by  $x_1 = \sqrt{\Sigma_1} \cdot a$ ; the extra atom contribution is  $\Delta$ ,  $(\Sigma_2)^{-1}$ ,  $\Sigma_2 = (z_3^2 + z_4^2)$  and  $x_2$ , respectively. The resulting double doping is given by  $(\Sigma_3)^{-1}$ ,  $\Sigma_3 = (z_9^2 + z_{10}^2)$  and  $x_3$  represents positions with unit cells containing both. Point matching for the two doping patterns projected into the superconducting plane, as illustrated in Fig. 2, is leading to

$$(z_1^2 + z_2^2) \cdot (z_5^2 + z_6^2) = (z_3^2 + z_4^2) \cdot (z_7^2 + z_8^2) = (z_9^2 + z_{10}^2) \quad (2)$$

The compound  $\text{La}_{2-\Delta}\text{Ca}_{1+\Delta}\text{Cu}_2\text{O}_{6+\delta}$  has been investigated on superconducting and non-superconducting in the range  $0.08 \leq \Delta \leq 0.25$  with an optimum at  $\Delta = 0.18$  [7,8,11] and a density of  $(\Sigma_2)^{-1} = [1 - 2.82/3.00] \equiv 6\%$ . According to our concept of a uniform doping projection into the  $\text{CuO}_2$  plane, the reciprocal value should be a square number for the simplest and uniform distribution or the sum of two square numbers. For the simplest case we have  $\Sigma_2 = 16.66 \approx 16 = (z_3^2 + z_4^2) = 4^2 + 0^2 \equiv 6.25\%$  leading to a doping distance of  $x_2 = \sqrt{16} \cdot a = 1.53 \text{ nm}$ .

Systematic research of the optimum oxygen content has been performed by several authors [7,8]. The highest  $T_c$  has been achieved by synthesizing  $\text{La}_{2-\Delta}\text{Ca}_{1+\Delta}\text{Cu}_2\text{O}_{6+\delta}$  under 400 atm oxygen partial pressure leading to a value of  $\delta = 0.02$ . This results in a density for half O-atoms of  $(\Sigma_1)^{-1} = [1 - 6.00/(6.00 + 2\delta)] \equiv 0.66\% \approx 0.7\%$  with  $\Sigma_1 \approx 140 - 150$ . For the simplest case the nearest square number is  $144 = (z_1^2 + z_2^2) = 12^2 + 0^2$  so that the doping distance is given by  $x_1 = 12 \cdot a = 4.60 \text{ nm}$ .

If the uniform doping pattern of the unit cells with extra  $\text{Ca}^{2+}$ -ions and the oxygen excess atom causes the superconducting process, then the doping distance is given by point matching between the two doping patterns — Ca-atom and O-atom distribution. Therefore, the requirement  $(z_1^2 + z_2^2)/(z_3^2 + z_4^2) = (z_7^2 + z_8^2)$  leads to  $144/16 = 9 = 3^2 + 0^2$  with a resonance distance

of  $x_1 = x_3 = 12 \cdot a = 4.60 \text{ nm}$  and a HTSC unit area of  $A_{SC} = 144 \cdot \text{CuO}_2$ , as illustrated in Fig. 2 and summarized in Table 1.  $\Sigma_3 = 144$  is the least common multiple of  $\Sigma_1 = 144$  and  $\Sigma_2 = 16$ , so that  $z_5 = 1$  and  $z_6 = 0$ .

Eq. (2) provides a very strict/stringent instruction for the matching and is very sensitive to the experimental doping values.

#### 4. Discussion

As already pointed out in publication [4], the critical transition temperature  $T_c$  should increase with the number of superconducting  $\text{CuO}_2$  planes per chemical formula by  $T_c \sim n^{2/3}$ . This is analogous to the relation between the Fermi energy  $E_F$  and the carrier density  $N_c$  given by  $E_F \sim (n \cdot N_c)^{2/3}$ , which has the dimension of  $(\text{area})^{-1}$ . The Fermi energy equation

$$E_F = h^2 / (8M_{\text{eff}}) \cdot (n \cdot N_c)^{2/3} \cdot (3/\pi)^{2/3} \quad (3)$$

could be rewritten, with the assumption that the carrier distance is given by  $(N_c)^{-1/3} = x$  and  $(3/\pi)^{-2/3} = 1.0312 \approx 1$ , to

$$4 \cdot x^2 \cdot n^{-2/3} \cdot 2M_{\text{eff}} \cdot E_F \approx h^2 \quad (4)$$

which is very similar to Eq. (1).

The calculated transition temperature  $T_c$  (calc.) = 52.2 K according to Eq. (1) compares well with the different experimental values in the range of  $T_c = 52.4 \pm 1 \text{ K}$  [7,8,11], which are considered to be taken at half of the transition interval of the resistivity–temperature curves. In the referenced literature they are sometimes denoted as the middle temperature.

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