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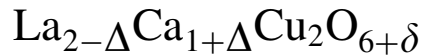
Acta Astronautica 65 (2009) 1179–1183



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ACADEMY TRANSACTIONS NOTE

Doping structure of the high temperature superconductor



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Received 7 February 2009; accepted 10 March 2009

Available online 15 April 2009

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 CuO_2 planes per chemical formula. The distance x between double doped unit cells projected into a CuO_2 plane matches the experimental transition temperature T_c quite well.

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Keywords: High temperature superconductors; Superconducting unit area

1. Introduction

The ternary compound La_2CuO_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 CuO_2 planes per chemical formula ($n > 1$) offer even higher critical transition temperatures T_c than single 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- CuO_2 -layer compound ($n = 2$) is doped with Ca-atoms and also with oxygen excess.

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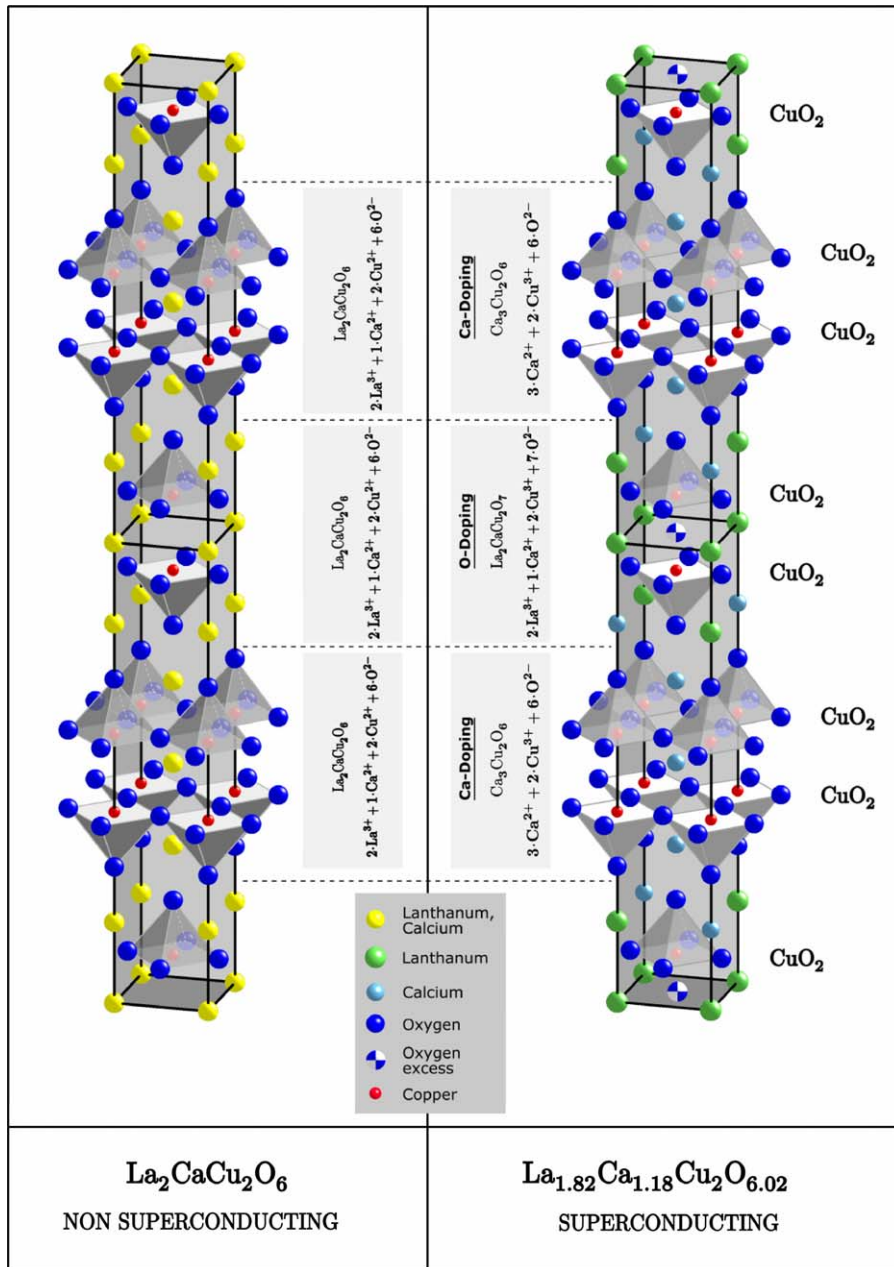


Fig. 1. Crystal structure and electronic arrangement of non-superconducting and superconducting $\text{La}_{2-\Delta}\text{Ca}_{1+\Delta}\text{Cu}_2\text{O}_{6+\delta}$.

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 Ca^{2+}

(0.099 nm) is smaller than for La^{3+} (0.106 nm) and 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 (6O^{2-}) need 12 electrons which are provided by $2\text{La}^{3+} + 1\text{Ca}^{2+} + 2\text{Cu}^{2+}$. This material has no Cu^{3+} -element and is not superconducting unless La^{3+} is substituted by Ca^{2+} and the material is doped by an appropriate oxygen excess

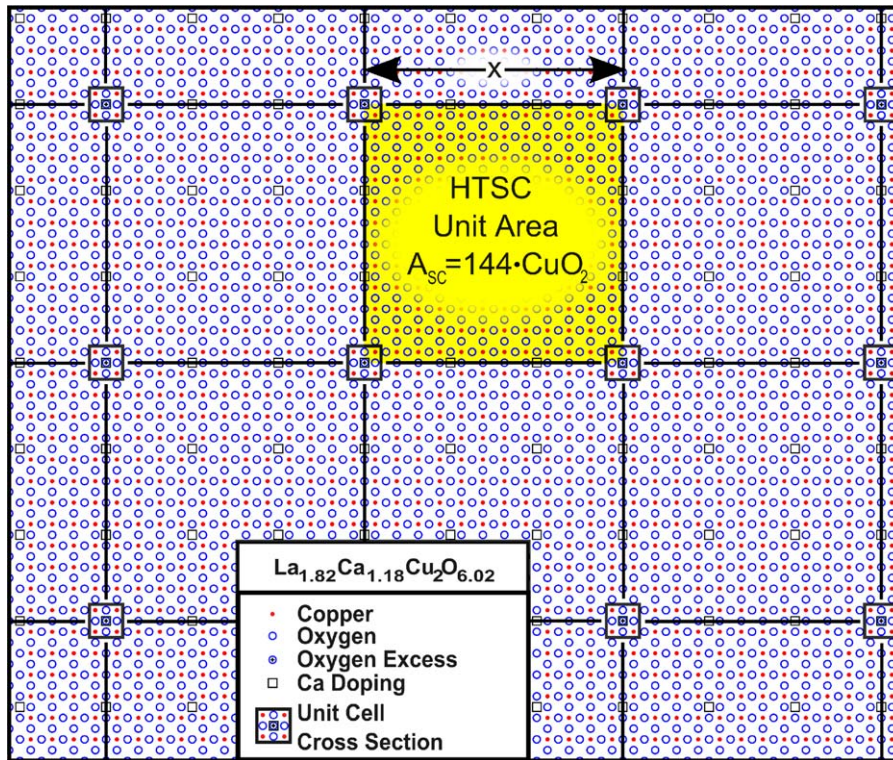


Fig. 2. Superconducting CuO_2 plane of $\text{La}_{1.82}\text{Ca}_{1.18}\text{Cu}_2\text{O}_{6.02}$ (LCCO-52) with a T-crystal structure ($a = b = 0.383 \text{ nm}$). The distance between double doped unit cells is the superconducting resonance length $x = 4.60 \text{ nm}$. The superconducting unit area 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 CuO_2 planes and the extra O-atom forms a cluster with La^{3+} -ions at that position and
- (b) 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 CuO_2 planes originally containing Cu^{2+} -ions. The introduction of an extra O-atom between the two CuO_2 planes takes one extra electron from above and one from below.

Therefore, we only need half an O-atom per 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 Δ 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 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)	$(2x_3)^2 \cdot n^{-2/3} \times 10^{-18}$ (m^2)	T_c calc. (K)
			δ	$(\Sigma_1)^{-1}$ (%)	x_1 (nm)	Δ	$(\Sigma_2)^{-1}$ (%)	x_2 (nm)			
$\text{La}_{2-\Delta}\text{Ca}_{1+\Delta}\text{Cu}_2\text{O}_{6+\delta}$ LCCO-52	52.4 ± 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 δ , its density by $(\Sigma_1)^{-1}$, the number of unit areas per doping atom within one 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 Δ , $(\Sigma_2)^{-1}$, $\Sigma_2 = (z_3^2 + z_4^2)$ 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 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 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 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.

References

- [1] M. Francois, K. Yvon, P. Fischer, M. Decroux, Structural phase transition at 150 K in the high-temperature superconductor $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$, Solid State Commun. 63 (1) (1987) 35–40.
- [2] M. Reehuis, C. Ulrich, K. Prokes, A. Gozar, G. Blumberg, S. Komiyama, Y. Ando, P. Pattison, B. Keimer, Crystal structure and high-field magnetism of La_2CuO_4 , Phys. Rev. B 73 (2006) 144513.

- [3] H.P. Roeser, F. Hetfleisch, F.M. Huber, M.F. von Schoenermark, M. Stepper, A. Moritz, A.S. Nikoghosyan, A link between critical transition temperature and the structure of superconducting $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$, *Acta Astronaut.* 62/12 (2008) 733–736.
- [4] H.P. Roeser, F. Hetfleisch, F.M. Huber, M.F. von Schoenermark, M. Stepper, A. Moritz, A.S. Nikoghosyan, Correlation between oxygen excess density and critical transition temperature in superconducting Bi-2201, Bi-2212 and Bi-2223, *Acta Astronaut.* 63 (2008) 1372–1375.
- [5] H.P. Roeser, F.M. Huber, M.F. von Schoenermark, A.S. Nikoghosyan, High temperature superconducting with two doping atoms in La-doped Bi-2201 and Y-doped Bi-2212, *Acta Astronaut.* (2009), doi:10.1016/j.actaastro.2009.02.004.
- [6] H.P. Roeser, F.M. Huber, M.F. von Schoenermark, A.S. Nikoghosyan, F. Hetfleisch, M. Stepper, A. Moritz, Doping Patterns in N-Type High Temperature Superconductors PLCCO and NCCO, *Acta Astronaut.* (2009), doi:10.1016/j.actaastro.2009.01.053.
- [7] K. Kinoshita, T. Yamada, Superconductivity and antiferromagnetism in $\text{La}_{2-x}\text{Ca}_{1+x}\text{Cu}_2\text{O}_{6 \pm \delta}$ and $\text{La}_{2-x}\text{Sr}_x\text{CaCu}_2\text{O}_{6 \pm \delta}$, *Phys. Rev. B* 46 (14) (1992) 9116–9122.
- [8] D. Jung, The role of oxygen for expressing superconductivity in La–Ca–Cu–O compounds, *Bull. Korean Chem. Soc.* 20 (3) (1999) 281–284.
- [9] A. Fuertes, X. Obradors, J.M. Navarro, P. Gomez-Romero, N. Casan-Pastor, F. Perez, J. Fontcuberta, C. Miravittles, J. Rodriguez-Carvajal, B. Martinez, Oxygen excess and superconductivity at 45 K in $\text{La}_2\text{CaCu}_2\text{O}_{6+y}$, *Physica C* 170 (1990) 153–160.
- [10] M. Hücker, Y.J. Kim, G.D. Gu, J.M. Tranquada, B.D. Gaulin, J.W. Lynn, Neutron scattering study on $\text{La}_{1.9}\text{Ca}_{1.1}\text{Cu}_2\text{O}_{6+\delta}$ and $\text{La}_{1.85}\text{Sr}_{0.15}\text{CaCu}_2\text{O}_{6+\delta}$, *Phys. Rev. B* 71 (2005) 094510.
- [11] H. Shaked, J.D. Jorgensen, B.A. Hunter, R.L. Hitterman, K. Kinoshita, F. Izumi, T. Kamiyama, Defect structure and superconducting properties of $\text{La}_{1.8}\text{Sr}_x\text{Ca}_{1.2-x}\text{Cu}_2\text{O}_{6-\delta}$, *Phys. Rev. B* 48 (17) (1993) 12941–12950.
- [12] C. Ulrich, S. Kondo, M. Reehuis, H. He, C. Bernhard, C. Niedermeyer, F. Bouree, P. Bourges, M. Ohl, H.M. Ronnow, H. Takagi, B. Keimer, Structural and magnetic instabilities of $\text{La}_{2-x}\text{Sr}_x\text{CaCu}_2\text{O}_6$, *Phys. Rev. B* 65 (2002) 220507.