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High temperature superconducting with two doping atoms in La-doped Bi-2201 and Y-doped Bi-2212

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Abstract

These crystals have two doping patterns given by oxygen excess and doping with an additional atom with projected positions in the CuO_2 plane. Both doping elements are necessary for the occurrence of superconductivity. Where the two doping patterns overlap, the point matched locations act as the resonating superconducting pathway and might explain a correlation between T_c and the doping structure.

Keywords: High temperature superconductors; Superconducting unit area; Superconducting current channels

1. Introduction

In cuprates, the CuO_2 plane is a highly symmetrical and a very well ordered system. Bonding lengths and planarity are very well known by X-ray and neutron diffraction experiments. The superconducting process requires the existence of Cu^{3+}-ions in these planes as well as homogeneously distributed oxygen deficiency or excess positions in or near the CuO_2 planes. In previous papers [1–4] a strong correlation has been found between the doping distances (x) and the critical transition temperatures T_c. However, there exist many high temperature superconductors (HTSC) that have an extra doping atom, in addition to the oxygen excess atom.

In this paper we will analyse if double doped cuprates also follow the correlation Eq. (1) between the doping structure value $(2x)^2$ and T_c. We have chosen the cuprates La-doped Bi-2201 and Y-doped Bi-2212 which are HTSCs with oxygen excess atoms [2]:

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

2. Geometry in the superconducting CuO_2 plane with two doping atoms

For double doped HTSCs, the concept of the unit area for one doping element [1–4] needs to be extended for two different doping elements. The oxygen excess contribution is given by δ, its density by $(\Sigma_1)^{-1}$, the number of unit cells per doping atom within the CuO_2 plane by Σ_1 and the density distance by x_1; the extra atom contribution is Δ, $(\Sigma_2)^{-1}$ and x_2, respectively, and the resulting double doping, which is a match between

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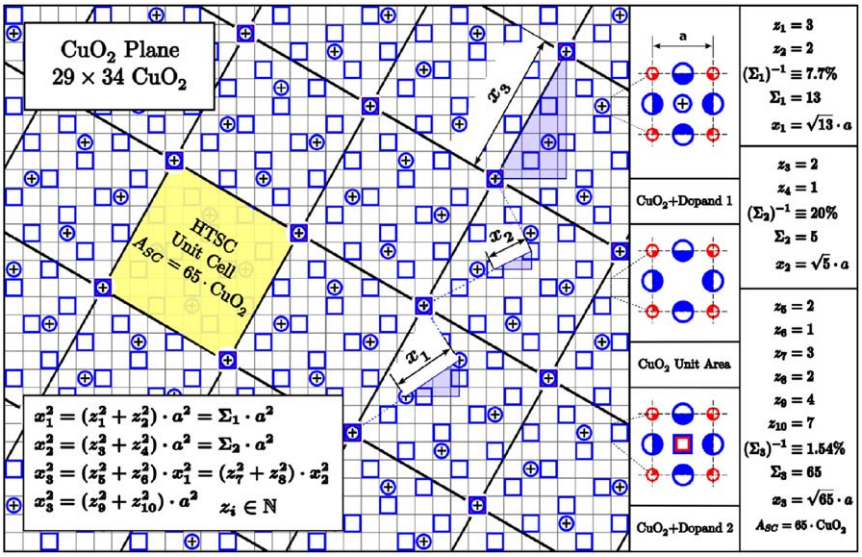

Fig. 1. Illustration of a double doped cuprate where the positions of CuO_2 unit areas representing a unit cell which contains two doping atoms are given by a point matching for the two doping patterns which is similar to a Moiré effect.

the oxygen excess positions and the extra atom positions, is given by $(\Sigma_3)^{-1}$ and x_3.

Cuprates have a tetragonal unit cell structure and the CuO_2 unit area has a symmetrical Cu- and O-atom distribution so that all directions for the superconducting carrier flow should be permitted. As an example, Fig. 1 illustrates the concept for an arbitrary section of the CuO_2 plane with $[29 \cdot 34]$ CuO_2 unit areas filled with two different homogeneously distributed dopants. The distances (x_i) are given by the hypotenuse of right triangles with $x_i = \sqrt{\Sigma_k} \cdot a$ and $\Sigma_k = {z_i}^2 + {z_j}^2$ with $z_{i,j} \in \mathbb{N}$, because of the highly periodic and square pattern of the CuO_2 plane. The positions of CuO_2 unit areas containing two doping atoms are given by a point matching for the two doping patterns which is similar to a Moiré effect leading to

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

$$\begin{matrix} (4^2 + 7^2) & (1^2 + 0^2) & = & (2^2 + 1^2) & (3^2 + 2^2) & = & (4^2 + 7^2) \\ 65 & 1 & = & 5 & 13 & = & 65 \end{matrix} \quad (2a)$$

The values for z_1 through z_4 will be given by the experimentally derived doping values δ and Δ or Σ_1 and Σ_2, respectively. For the numbers z_5 through z_{10} we are looking for the smallest number because the shortest distance is responsible for the highest T_c according to Eq. (1). Eq. (2a) represents the numerical values for Bi-2201-La. For the known HTSCs, the doping level values δ and Δ are larger than $(\Sigma_k)^{-1} \equiv 0.5\%$ leading to values of $\Sigma_k = {z_i}^2 + {z_j}^2 \leqslant 200$ for $k = 1, 2$.

3. $Bi_2Sr_{1.6}La_{0.4}CuO_{6+\delta}$ (Bi-2201-La)

The parent compound $Bi_2Sr_2CuO_6$ (Bi-2201), shown in Fig. 2, is not superconducting. When an extra O-atom is added, the overdoped material $Bi_2Sr_2CuO_{6+\delta}$ is not superconducting either, because of the missing Cu^{3+}-ions in the CuO_2 plane [2]. Cu^{3+}-ions are created using Bi-2201 with oxygen excess and replacing Sr^{2+}-ions by trivalent ions like La^{3+}, Pr^{3+}, Nd^{3+}, Sm^{3+}, Eu^{3+}, Gd^{3+} at a specific doping level [5]. In this way, the electronic arrangement in the unit cell, containing an excess O-atom and an La-atom, should read $2Bi^{3+}+1La^{3+}+1Sr^{2+}+1Cu^{3+}+7O^{2-}$ with a chemical formula $Bi_2Sr_{1-\Delta}La_{\Delta}CuO_{6+\delta}$. It has been demonstrated that at an optimum La-doping value of $\Delta = 0.4$ a transition temperature of $T_c = 35.5 \pm 2.5\,\mathrm{K}$ can be measured [5–7]. For Bi-2201 it is difficult to obtain high quality single crystals, which explains the large variation of experimental T_c values. According to equations in Fig. 1, the value $\Delta = 0.4$ leads to $(\Sigma_2)^{-1} = (1 - 1.6/2.0) \equiv 20\%$ and $\Sigma_2 = 5 = 2^2 + 1^2 = {z_3}^2 + {z_4}^2$ with a doping distance of $x_2 = \sqrt{5} \cdot a = 1.21\,\mathrm{nm}$ (Table 1).

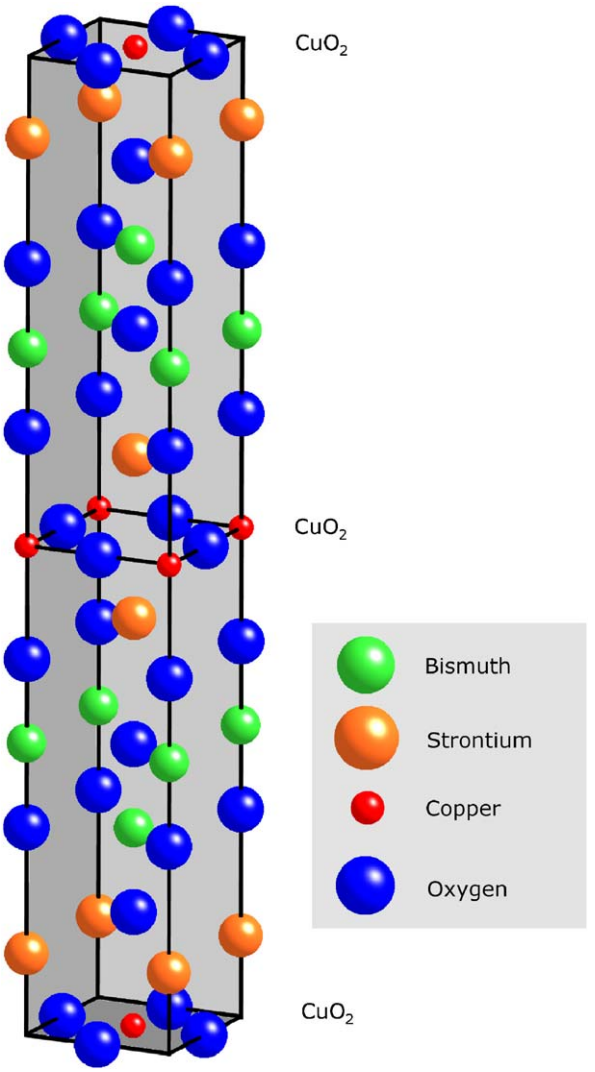

Fig. 2. The unit cell of Bi-2201 consists of $2 \cdot [Bi_2Sr_2CuO_6]$ and has two CuO_2 planes. Note the alternate displacement of the stacking sequence of CuO_2 planes.

Superconductivity in the Bi-family requires a very low oxygen excess which is achieved with an appropriate annealing process. The preparation for Bi-2201 is done at temperatures between 650 and 800 °C within a low oxygen atmosphere and over a long time [5,8,9]. It has been shown that the composition of Bi-2201 follows the nominal compositions in Bi-2212 [5].

Superconductivity is achieved with a value of $\delta \approx 0.1$ with an oxygen content of about $(\Sigma_1)^{-1} = (1-6.0/6.1) \equiv 1.6 \pm 0.25\%$ [8]. The condition given by Eq. (2) that $\Sigma_1 = (z_1{}^2+z_2{}^2)$ permits only certain numbers for Σ_1 (58, 61, 64, **65**, 68, 72, 73, 74), but since

Table 1
Correlation between experimental and calculated transition temperatures in double doped Bi-2201 and Bi-2212 high temperature superconductors.

Material	T_c (K) exp.	Crystal structure (nm)	Oxygen excess distance			Atomic doping		Carrier distance x_3 (nm)	$(2x_3)^2 \cdot n^{-2/3}$ 10^{-18} (m^2)	T_c (K) calc.
			δ	$(\Sigma_1)^{-1}$ (%)	x_1 (nm)	Δ	$(\Sigma_2)^{-1}$ (%)	x_2 (nm)		
$Bi_2Sr_{2-\Delta}La_\Delta CuO_{6+\delta}$ Bi-2201-La	35.5 ± 2.5	$a = 0.541$, $c = 2.5$	~0.1	~1.6	4.36	0.4	20.0	1.21	4.36; $A_{sc} = 65 \cdot CuO_2$	76.1 ($n = 1$)	36.5
$Bi_2Sr_2Ca_{1-\Delta}Y_\Delta Cu_2O_{8+\delta}$ Bi-2212-Y91	91 ± 1	$a = 0.541$, $c = 3.08$	0.16	3.85	2.76	~0.08	7.7	1.95	2.76; $A_{sc} = 26 \cdot CuO_2$	30.4 ($n = 1$)	91.2
$Bi_2Sr_2Ca_{1-\Delta}Y_\Delta Cu_2O_{8+\delta}$ Bi-2212-Y95	95 ± 1	$a = 0.541$, $c = 3.08$	0.16–0.17	4 ± 0.15	2.70	0.08	8.0	1.91	2.70; $A_{sc} = 25 \cdot CuO_2$	29.2 ($n = 1$)	95.2

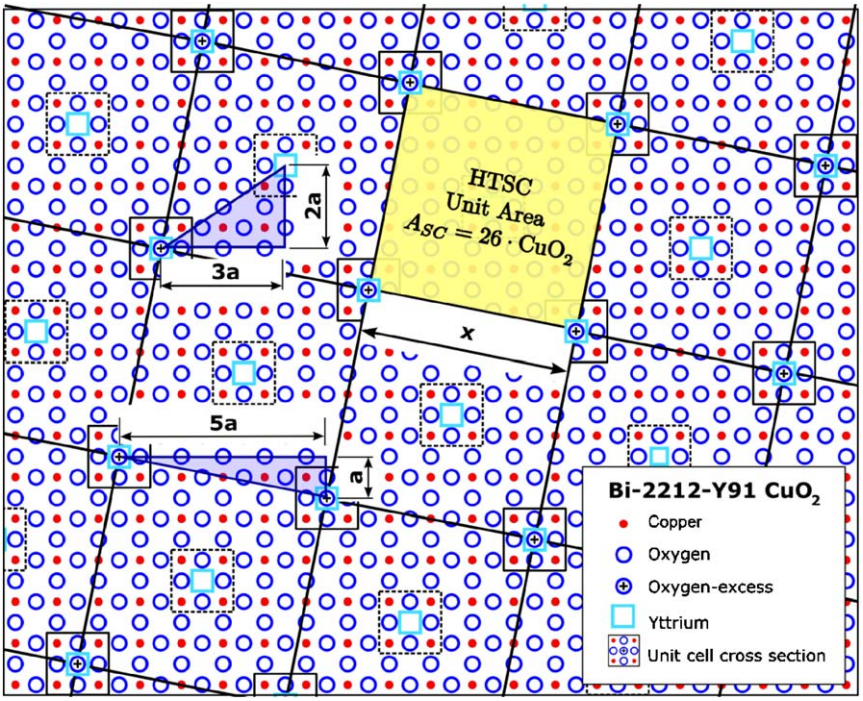

Fig. 3. Superconducting CuO_2 plane of Bi-2212-Y91 ($a \approx b = 0.541$ nm). The distance between oxygen excess atoms is the superconducting resonance length $x = 2.76$ nm. The superconducting unit area has the size of $26 \cdot CuO_2$ unit areas.

$(z_1{}^2+z_2{}^2)/(z_3{}^2+z_4{}^2) = (z_1{}^2+z_2{}^2)/5 = z_i$, then $\Sigma_1 = 65$ is the only solution, which is equivalent to $(\Sigma_1)^{-1} \equiv 1.54\%$. This calculation can be solved with a simple computer program using the conditions of Eq. (2) and leads to the solution of a rectangular pattern with $x_1 = x_3 = \sqrt{65} \cdot a = 4.36$ nm (Table 1) and a HTSC unit area of $A_{SC} = 65 \cdot CuO_2$ (Fig. 1).

4. $Bi_2Sr_2Ca_{1-\Delta}Y_\Delta Cu_2O_{8+\delta}$ (Bi-2212-Y)

The electronic arrangement for pure $Bi_2Sr_2CaCu_2O_{8+\delta}$ (Bi-2212) in the unit cell with an excess oxygen atom is $2Bi^{3+}+1Ca^{2+}+2Sr^{2+}+2Cu^{3+}+9O^{2-}$. This compound forms two superconducting CuO_2 planes in which the hole doped cuprate possesses an effective mass of $M_{eff} = 2m_e$. The highest transition temperature for the pure Bi-2212 published so far is $T_c = 82.5\,K \pm 0.5\,K$ [5,10] and has an oxygen excess of $\delta = 0.18$ [2]. Reports have been published demonstrating a maximum transition temperature in the range of $T_c = 90-96\,K$ for so-called "optimized doping" levels with a value of about $\delta = 0.16$. In those cases, Bi-2212 has been additionally doped with a small amount of yttrium or other atoms to yield a well-ordered system [5]. In analysing the published results, there are two different critical transition temperature levels, one at $T_c = 91 \pm 1\,K$ for a Y-doping level of about $\Delta = 0.08$ resulting in $Bi_2Ca_{0.92}Sr_2Y_{0.08}Cu_2O_{8+\delta}$ [10–13]. The second transition is at $T_c = 95 \pm 1\,K$ for the same amount of yttrium but somewhat higher oxygen excess doping level [5,14,15].

4.1. Bi-2212-Y91

For the Y-doped case, one chemical formula has two CuO_2 planes plus two SrO and two BiO planes and a Y-atom in the middle of the unit cell between the two CuO_2 planes. Detailed measurements have been done to optimize the oxygen excess doping, resulting in $\delta = 0.16$ [16] for $T_c = 91\,K$. If the oxygen excess atom is located only between the two CuO_2 planes then the relevant density is $O_{4.16}$ instead of $O_{8.16}$ leading to $(\Sigma_1)^{-1} = (1-4.00/4.16) \equiv 3.85\%$, so that $\Sigma_1 = 26 = 5^2+1^2 = z_1{}^2+z_2{}^2$. The doping distance is then $x_1 = \sqrt{26} \cdot a = 2.76$ nm. The electronic arrangement at the position, where we find an oxygen excess atom and a Y-atom at the same time, is given by $2Bi^{3+}+Y^{3+}+2Sr^{2+}+Cu^{2+}+Cu^{3+}+9O^{2-}$. This

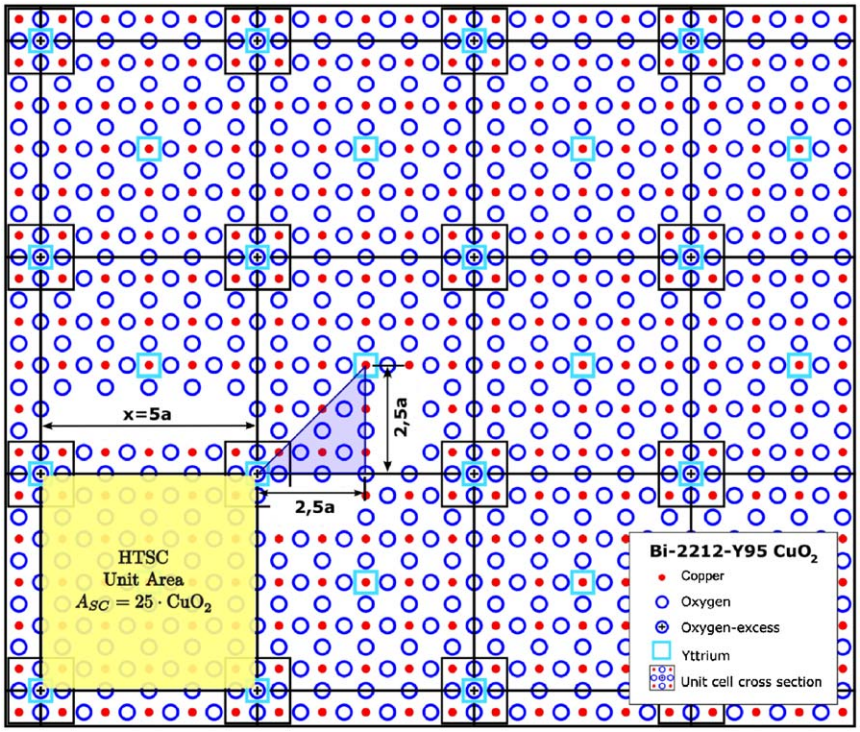

Fig. 4. Superconducting CuO_2 plane of Bi-2212-Y95 ($a \approx b = 0.541$ nm). The distance between oxygen excess atoms is the superconducting resonance length $x = 2.70$ nm. The superconducting unit area has the size of $25 \cdot CuO_2$ unit areas.

indicates that only one CuO_2 plane will be superconducting, resulting in $n = 1$ for Eq. (1) as is the situation with $YBa_2Cu_3O_{7-\delta}$ [1]. For an yttrium level of about $\Delta = 0.08$, the density is $(\Sigma_2)^{-1} = (1-0.92/1.00) \equiv 8\%$ so that $\Sigma = 12.5 \approx 13 = 3^2+2^2 = {z_3}^2+{z_4}^2$. This results in a doping distance of $x_2 = \sqrt{13} \cdot a = 1.95$ nm. The Moiré requirement according to Eq. (2) results in $z_5 = z_6 = z_7 = 1$ and $z_8 = 0$ illustrated in Fig. 3 with $x_3 = x_1 = 2.76$ nm and a HTSC unit area of $A_{SC} = 26 \cdot CuO_2$. The calculated transition temperature T_c (calc.) = 91.2 K compares well with the experimental derived values.

4.2. Bi-2212-Y95

For this material, the oxygen doping level is only slightly higher, with a value of $\delta = 0.16-0.17 \approx 16.5$ resulting in $(\Sigma_1)^{-1} \equiv 4\%$, so that $\Sigma_1 = 25 = 5^2+0^2$ and the doping distance results in $x_1 = \sqrt{25} \cdot a = 2.70$ nm. The Y-atom content has been determined very accurately to 8% which yields an yttrium distribution as illustrated in Fig. 4 and a HTSC unit area of $A_{SC} = 25 \cdot CuO_2$.

5. Discussion

The calculated transition temperatures compare well with the experimental data and match Eq. (1) results and fit on the correlation curve in [2]. This result supports the suggestion that the superconducting CuO_2 highway contains superconducting current channels where carriers are moving parallel and in phase at the same velocity. Further analysis could determine if Eq. (1) could be derived from the density of states in a 1D quantum wire [17].

Pure $Bi_2Sr_2CaCu_2O_{8+\delta}$ (Bi-2212) has a transition temperature of $T_c = 82.5$ K, but if it is doped with Y-atoms it reaches $T_c = 91-95$ K. This T_c value is very similar to $YBa_2Cu_3O_{7-\delta}$ with $T_c = 93$ K [1]. Similarly, La-doped $Bi_2Sr_{1.6}La_{0.4}CuO_{6+\delta}$ has a $T_c = 36.5$ K and $La_{1.85}Sr_{0.15}CuO_4$ (LSCO) displays $T_c = 35$–40 K. Obviously the dopants yttrium and lanthanum determine the maximum transition temperature by increasing

(Y-atom) or decreasing (La-atom) the maximum carrier velocity as suggested in [1–4].

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