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Doping patterns in N-type high temperature superconductors PLCCO and NCCO

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Abstract

It has been demonstrated that the correlation between the doping distance and the critical transition temperature T_c for P-type HTSCs also applies to double doped N-type HTSCs. It is suggested that electron doped HTSCs also form superconducting current channels lying parallel in the CuO_2 plane.

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1. Introduction

Most of the high temperature superconductors (HTSC) are hole-doped compounds based on copper oxide and iron oxide. Shortly after the discovery of hole-doped HTSCs, another copper oxide family was discovered in which the carriers are electrons instead of holes [1,2]. These HTSCs with the chemical formulas $\text{Pr}_{1-\Delta}\text{LaCe}_\Delta\text{CuO}_{4-\delta}$ and $\text{Ln}_{2-\Delta}\text{Ce}_\Delta\text{CuO}_{4-\delta}$ are Ce^{4+} -doped compounds, where Ln stands for lanthanides Pr, Nd, La, Sm and Eu having transition temperatures T_c below 30K. Their undoped parent compounds PrLaCuO_4 and e.g. Nd_2CuO_4 have a so-called

T' -phase crystal structure (Fig. 1). Compared to hole-doped HTSCs, the T' -structure has no apical O-atom above and/or below the CuO_2 -plane and cannot be doped with holes. This has been confirmed by measurements of negative Hall and negative Seebeck coefficients [3]. Both P-type and N-type HTSCs are working with an effective mass of $M_{\text{eff}} = 2m_e$.

In this paper we will analyse if electron-doped single layer ($n=1$) cuprates also follow the correlation of Eq. (1) between the doping structure value $(2x)^2$ and T_c [4,5]. We have chosen the N-type cuprates $\text{Pr}_{1-\Delta}\text{LaCe}_\Delta\text{CuO}_{4-\delta}$ (PLCCO) and $\text{Nd}_{2-\Delta}\text{Ce}_\Delta\text{CuO}_{4-\delta}$ (NCCO) with Ce^{4+} doping and oxygen deficiency, because they have been studied in great detail.

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

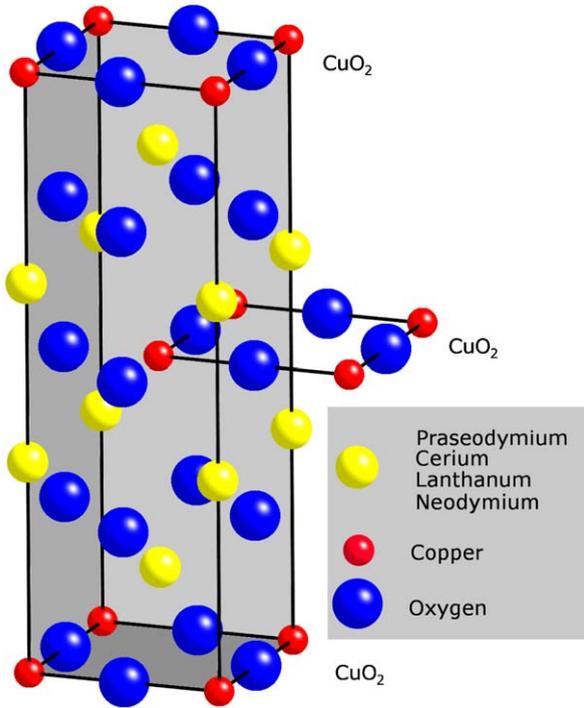


Fig. 1. PLCCO and NCCO are N-type HTSCs and have a T' -phase unit cell. One Nd-atom in NCCO or Pr-atom in PLCCO can be substituted by a Ce-atom in the second or fourth layer of the unit cell.

2. Double doping in cuprates

The double doping concept has been described in the case of oxygen excess and additional atoms like Y-atoms and La-atoms [3], so we will use the same procedure for the case of oxygen deficiency. The oxygen deficiency contribution is given by δ , its density by $(\Sigma_1)^{-1}$, the number of unit areas per doping atom within the CuO_2 plane by Σ_1 and the density distance by x_1 ; the extra atom contribution is given by Δ , $(\Sigma_2)^{-1}$ and x_2 , respectively. The resulting double doping is given by $(\Sigma_3)^{-1}$ and x_3 representing positions with unit cells containing both. It is a point matching for the two doping patterns projected into the superconducting plane, as illustrated in Fig. 2, leading to

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

The process of oxygen reduction creates oxygen vacancies in stoichiometric CuO_2 planes for PLCCO and NCCO and injecting mobile electrons into the superconducting CuO_2 layer [6]. Therefore, we project the density distribution of the Ce^{4+} -ions into the CuO_2 plane and the doped unit areas in Fig. 2 represent a complete chemical formula which is half of a unit cell.

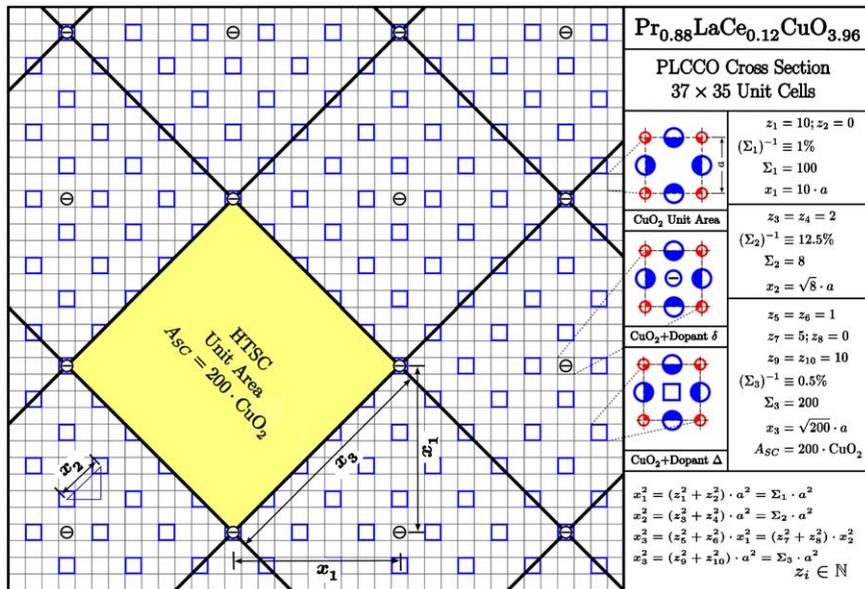


Fig. 2. Superconducting CuO_2 plane of PLCCO ($a = b = 0.398$ nm). The distance between double doped unit cells is the superconducting resonance length $x = 5.63$ nm. The superconducting unit area has the size of $200 \cdot \text{CuO}_2$ unit areas.

3. Pr_{0.88}LaCe_{0.12}CuO_{3.96} (PLCCO)

The N-type HTSC material Pr_{1-Δ}LaCe_ΔCuO_{4-δ} has a tetragonal unit cell (space group I4/mmm) with the dimensions $a = b = 0.398$ nm and $c = 1.227$ nm (Fig. 1) which consists of $2 \cdot [\text{Pr}_{1-\Delta}\text{LaCe}_\Delta\text{CuO}_{4-\delta}]$. Using single crystals, a transition temperature in the range of $T_c = 22 \pm 2$ K has been reported by many research groups when optimizing the doping concentration of cerium and oxygen deficiency to $\Delta = 0.12$ and $\delta = 0.04$ [6–10], respectively.

The transition temperatures T_c for PLCCO and NCCO are considered to be taken at half of the transition when analysing the resistivity–temperature curves. The variation of e.g. ± 2 K for PLCCO represents the spread/deviation of different experimental results when using single crystals only. For very thin superconducting films the transition temperature could be about 1 K higher or lower depending on the substrate material for the films.

The parent compound PrLaCuO₄ is not superconducting, because the electronic arrangement Pr³⁺+La³⁺+Cu²⁺+4O²⁻ does not contain Cu³⁺ -ions, as is the case for most of the P-type cuprates. When doping with Ce-atoms, the electronic arrangement of the unit cell, where the Pr-atom has been replaced by a Ce-atom, is La³⁺+Ce⁴⁺+Cu¹⁺+4O²⁻ and provides no superconductivity either. The Cu²⁺ is transformed into Cu¹⁺ because the preferred ionization for cerium is Ce⁴⁺, the result of the 4f¹5d¹6s² electron configuration and the lower ionization energy compared to Cu³⁺. Additional “doping” with oxygen deficiency results in a unit cell with a Ce-atom and a missing O-atom and an electronic arrangement of La³⁺+Ce⁴⁺+Cu¹⁺+3O²⁻+2e⁻ which provides two free electrons and transforms the material into a N-type HTSC.

An oxygen deficiency with $4-\delta = 3.960$ [7,8] results in a uniform doping with positions where an oxygen atom is missing with $(\Sigma_1)^{-1} = (1-3.960/4.0) \equiv 1\%$ and $\Sigma_1 = 100 = 10^2 + 0^2 = (z_1^2 + z_2^2)$. Superconductivity shows up at an optimized ratio of cerium to praseodymium at $\Delta = 0.12$ with $(\Sigma_2)^{-1} = 0.12/1.0 \equiv 12\%$ and $\Sigma_2 = 8.3 \approx 8.0 = (z_3^2 + z_4^2) = 2^2 + 2^2 \equiv 12.5\%$ of Ce-atoms. Therefore, the distance between two N-type positions with two extra electrons is given by $x_3 = \sqrt{200} \cdot a = 14.14 \cdot 0.398$ nm = 5.63 nm, where $\Sigma_3 = 200$ is the smallest common denominator of $\Sigma_1 = 100$ and $\Sigma_2 = 8$, as illustrated in Fig. 2. The calculated transition temperature T_c (calc) = 21.9 K according to Eq. (1) with $n = 1$ compares well with the experimental value of $T_c = 22 \pm 2$ K (Table 1).

Table 1
Experimental and calculated transition temperatures in double doped PLCCO and NCCO high temperature superconductors.

| Material | T_c (K) exp. | Crystal structure (nm) | Oxygen deficiency distance | | Atomic doping | | Carrier distance x_3 (nm) | $(2x_3)^2 \times 10^{-18}$ (m ²) | T_c (K) calc. | |
|--|-------------------|----------------------------|----------------------------|--------------------------|---------------|----------|--------------------------------|---|--------------------|--------------------------|
| | | | δ | $(\Sigma_1)^{-1}$ (%) | x_1 (nm) | Δ | | | | $(\Sigma_2)^{-1}$ (%) |
| Pr _{1-Δ} LaCe _Δ CuO _{4-δ} PLCCO | 22 ± 2 | $a = 0.398$ $c = 1.227$ | 0.04 | 1 | 3.98 | 0.12 | 12.5 | 1.13 | 127 | 21.9 |
| Nd _{1.85} Ce _{0.15} CuO _{4-δ} NCCO-21 | 21.4 ± 0.5 | $a = 0.394$ $c = 1.207$ | 0.02 | 0.48 | 5.68 | 0.15 | 7.7 | 1.42 | 129 | 21.5 |
| Nd _{1.84} Ce _{0.16} CuO _{4-δ} NCCO-22 | 22.3 ± 0.5 | $a = 0.394$ $c = 1.207$ | 0.02 | 0.50 | 5.57 | 0.16 | 8.0 | 1.39 | 124 | 22.4 |

4. $\text{Nd}_{2-\Delta}\text{Ce}_{\Delta}\text{CuO}_{4-\delta}$ (NCCO)

The compound Nd_2CuO_4 has the same tetragonal unit cell as PLCCO with cell parameters $a = 0.394\text{ nm}$ and $c = 1.207\text{ nm}$ (Fig. 1) and becomes superconducting by Ce-substitution at Nd-sites when samples are properly annealed under reduced atmosphere. Several authors propose that heat treatment removes oxygen atoms at apical sites in as-grown samples, resulting in an injection of additional carriers by removing O^{2-} ions with an electronic arrangement of $\text{Nd}^{3+} + \text{Ce}^{4+} + \text{Cu}^{1+} + 3\text{O}^{2-} + 2e^-$. This provides two free electrons and transforms the material into a N-type HTSC. It has been observed that there is an abrupt onset and subsequent disappearance of superconductivity when the concentration of mobile electrons created by an oxygen deficiency is between $0.01 < \delta < 0.04$ [3,11–13]. The maximum transition temperature has been achieved at $\delta = 0.02$, which results in a uniform doping of missing oxygen atoms to $(\Sigma_1)^{-1} = (1 - 3.98/4.0) \equiv 0.5\%$ and $\Sigma_1 = 200 = 10^2 + 10^2 = (z_1^2 + z_2^2)$. The value Σ_1 could be slightly higher or lower, but must be equal to the sum of two square numbers and must match the Ce-atom content according to Eq. (2).

Most of the published T_c values are in the range of 21.5–22.7 K by using a Ce-atom contribution of $\Delta = 0.15$ –0.16 leading to a doping density between 7.5% and 8%.

For $\Delta = 0.15$ we have $(\Sigma_2)^{-1} = 0.15/2.00 \equiv 7.5\%$ with $\Sigma_2 = 13.3 \approx 13 = 2^2 + 3^2 = (z_3^2 + z_4^2)$ and a doping distance of $x_2 = \sqrt{13} \cdot a = 1.42\text{ nm}$. To match the oxygen deficiency the following requirement needs to be fulfilled: $(z_3^2 + z_4^2) \cdot (z_7^2 + z_8^2) \approx 200$. There is only one solution for a given Δ with $(2^2 + 3^2) \cdot (4^2 + 0^2) = 208 = (8^2 + 12^2)$ which results in an oxygen deficiency of 0.48% and is within the accuracy of the oxygen value. This leads to a doping distance of $x_3 = \sqrt{208} \cdot a = 5.68\text{ nm}$ and a calculated transition temperature of $T_c = 21.5\text{ K}$.

For $\Delta = 0.16$ we have $(\Sigma_2)^{-1} = 0.16/2.00 \equiv 8.0\%$ with $\Sigma_2 = 12.5 = 2.5^2 + 2.5^2 = (z_3^2 + z_4^2)$ and a doping distance of $x_2 = \sqrt{12.5} \cdot a = 1.39\text{ nm}$. In this case the distance can also be in multiples of half the unit cell size because we do not know if an Nd-atom in the second or fourth layer of the unit cell will be substituted by a Ce-atom. To match the oxygen deficiency the following requirement needs to be fulfilled: $(z_3^2 + z_4^2) \cdot (z_7^2 + z_8^2) \approx 200$. Again, there is only one solution for a given Δ with $(2.5^2 + 2.5^2) \cdot (4^2 + 0^2) = 200 = (10^2 + 10^2)$ which results

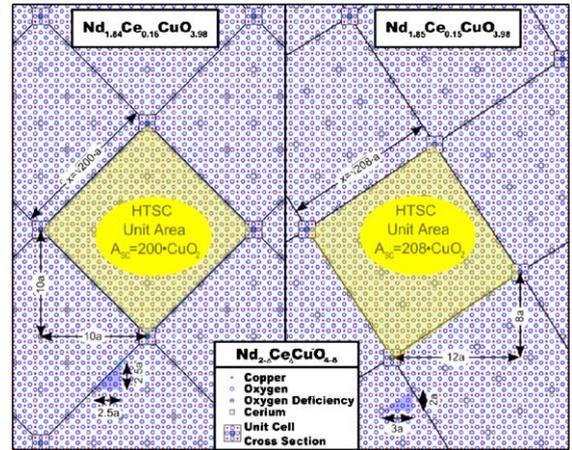


Fig. 3. Superconducting unit areas of NCCO in the CuO_2 plane ($a = b = 0.394\text{ nm}$). (a) For NCCO-21 the distance between double doped unit cells is the superconducting resonance length $x = 5.68\text{ nm}$. The superconducting unit area has the size of $208 \cdot \text{CuO}_2$ unit areas. (b) For NCCO-22 the superconducting resonance length is $x = 5.57\text{ nm}$ and the superconducting unit area has the size of $200 \cdot \text{CuO}_2$ unit areas.

in an oxygen deficiency of 0.50%. This leads to a doping distance of $x_3 = \sqrt{200} \cdot a = 5.57\text{ nm}$ and a calculated transition temperature of $T_c = 22.4\text{ K}$.

The Ce-atom content was not investigated with high accuracy by most of the authors. Therefore, we have illustrated both cases in Fig. 3 and refer for $\Delta = 0.16$ to $T_c = 22.3\text{ K}$ [14] and for $\Delta = 0.15$ to $T_c = 21.5\text{ K}$ [15] and $T_c = 21.3$ [16].

5. Discussion

The experimental T_c values of N-type HTSCs match the correlation curve of Eq. (1) for P-type HTSCs very closely (Fig. 4). The correlation curve has a slope of $m_1 = 2.77 \times 10^{-15}\text{ m}^2\text{ K}$ and an ordinate value of $+0.2 \times 10^{-18}\text{ m}^2$. These results support the resonance concept for HTSCs with an effective mass of $M_{\text{eff}} = 2m_e$ and carrying a charge of $Q = 2e^-$. Also for N-type HTSCs, superconducting charge carriers seem to be organized in parallel current channels or stripes within the CuO_2 -plane. It is interesting to note that the superconducting unit area pattern of PLCCO (Fig. 2) has a strong similarity to the single-crystal X-ray diffraction mesh scans in [6], which should be investigated further.

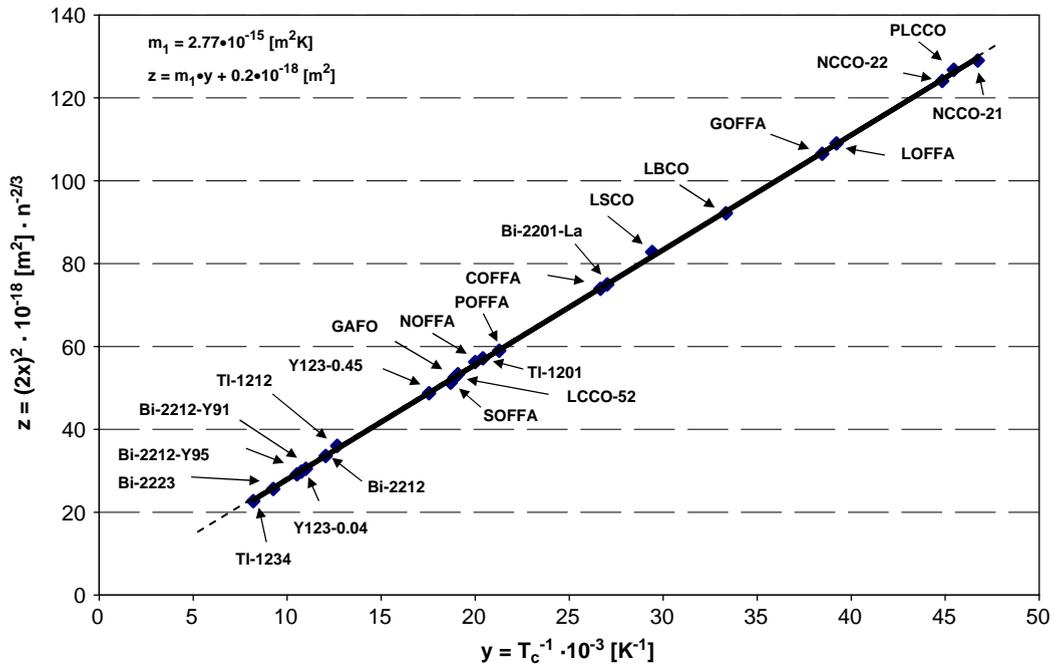


Fig. 4. Crystal geometry factor $(2x)^2$ of the superconducting plane versus the inverse critical transition temperature of different P- and N-type HTSCs. The value x is the doping distance and n represents the number of superconducting planes per chemical formula in the unit cell containing Cu^{3+} -ions in cuprates or Fe^{2+} -ions in iron-based HTSCs.

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