

# Determination of the critical temperature and oxygen content variations along the c-axis of YBCO epitaxial films

Yohann Thimont, Jean-François Hamet, Séverine Mouchel and Pierre Bernstein

CRISMAT-ENSICAEN et Université de Caen, Boulevard du Maréchal Juin F14050, Caen, France

E-Mail : pierre.bernstein@ensicaen.fr

**Abstract.** The existence of non-superconducting zones in  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  (YBCO) films below the transition temperature to the non-resistive state can be the cause of losses that limit the performances of YBCO devices. In this contribution, from the dependence on temperature of the surface critical current density of YBCO films we examine the possibility that their superconducting critical temperature, is non-uniform along their c-axis.

## 1. Introduction

While in classical superconductors the critical current density,  $j_{cr}(T)$ , is near its maximum for  $T = T_c/2$ , it is not the case in  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  (YBCO) films (see, for examples, the data reported in[1]). Although peculiarities in the transport properties of YBCO have been discussed for a long time and attributed to various causes [2], an interesting possibility is that  $j_{cr}(T)$  is non-uniform along the thickness of the sample because the critical temperature,  $T_c$ , and the oxygen content, [O], are also non-uniform along this direction.

In this contribution, from the dependence on temperature of the surface critical current density of c-axis oriented YBCO films,  $J_{cr}^S(T)$ , we examine the validity of the suggestion that there is a gradient in  $T_c$  and [O] along the films c-axis. The films were mostly made on  $\text{SrTiO}_3$  (STO) single crystals that, in some cases were coated with a  $\text{LaAlO}_3$  (LAO) buffer layer. Their surface critical current density was determined from magnetic moment measurements. The results are consistent with the picture of domains with different  $T_c$  stacked along the c-axis.

The paper is organized as follows. In section 2 we detail the making process of the films. In section 3 we describe how we have determined  $J_{cr}^S(T)$  from magnetic moment measurements and how we have established their  $T_c$  profiles. In section 4, we describe how we have built the  $T_c$ -[O] graphs. In Section 5 we consider some possible applications of this work.

## 2. Experimental Details

A large number of films were made in various conditions by Pulsed Laser Deposition (PLD) with an excimer laser ( $\lambda=248\text{nm}$ ). The samples were deposited either directly on a  $\text{SrTiO}_3$  substrate or on a  $\text{LaAlO}_3$  buffer layer deposited on a  $\text{SrTiO}_3$  substrate or, in one case, on a  $\text{LaAlO}_3$  substrate. All the substrates had a square shape with width  $w = 4\text{mm}$  or  $5\text{mm}$ . The thickness of the deposited films was in the  $90\text{nm}$ - $400\text{nm}$  range, the oxygen pressure during deposition was either  $0.5\text{mbar}$  or  $0.7\text{mbar}$  and the deposition temperature was in the  $740^\circ\text{C}$ - $760^\circ\text{C}$  range. At the end of the deposition step, pure oxygen was introduced in the vacuum chamber up to either  $500\text{mbar}$  or  $700\text{mbar}$ . Then, the samples were cooled down either at  $10^\circ\text{C}/\text{mn}$  or at  $20^\circ\text{C}/\text{mn}$  with, for some films, an oxygenation step either at  $300^\circ\text{C}$  or at  $600^\circ\text{C}$  for 30 minutes. For all the samples, X-rays diffraction diagrams show well marked peaks that correspond to the c-axis oriented YBCO phase with no indication of the presence of a-oriented YBCO.

### 3. Determination of the surface critical current density and of the $T_c$ profile of the films

#### 3.1 Magnetic measurements and determination of $J_{cr}^S(T)$

The films were cooled down to 20K in a cryostat. A  $H_a=0.5T$  field was applied perpendicular to the film plane, then switched off. The same procedure was carried out with a reverse field with the same amplitude. Then,  $m(T)$ , the magnetic moment of the sample, was measured with a SQUID device at increasing temperatures. The measured magnetic moment is due to currents persisting in the film after suppression of the applied field. According to Brandt and Indenbom, in a perpendicular field, the magnetic moment of a superconducting strip with length  $L$  and width  $w$  takes the form [3]

$$1. \quad m/L = -J_{cr}^S \frac{w^2}{4} \tanh(H_a/H_{cr}).$$

In Eq.(1),  $H_{cr}$  is the strip critical field. The  $\tanh\left(\frac{H_a}{H_{cr}}\right)$  term accounts for the field penetration in the sample. We have verified that no change was visible in the  $m(T)$  if excitation fields larger than 0.5T were applied. This suggests that the measured films were in the critical state at all the measurements temperatures and that the persisting currents flowed in the whole sample. Then, for  $L=w$ , from Eq.(1), we can write

$$2. \quad m(T) = -J_{cr}^S(T) w^3/4$$

and  $J_{cr}^S(T)$  can be calculated from the  $m(T)$  measurements.

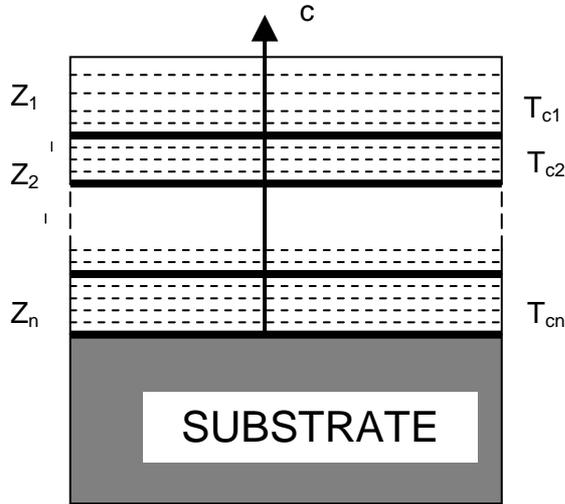
#### 3.2 Determination of the $T_c$ profiles

It is well known that YBCO films include boundary planes, i.e. twin boundaries and low angle grain boundaries, whose width is in the range of the superconducting coherence length [4]. This has led many authors to suggest the existence of tunneling pairs currents across the boundary planes [5,6,7,8]. However, the boundary planes also include a large number of defects with a size comparable to the coherence length [9,10]. The tunneling currents cannot flow across the boundary planes at the locations where, due to defects, the separation between both sides is large with respect to the coherence length. We have suggested that this results in the splitting of the boundary planes into rows of Josephson weak links [11,12] and established that  $J_{cr}^S(T)$ , for a YBCO film whose boundary planes include  $Z$  rows of Josephson weak links with the same  $T_c$ , takes the form

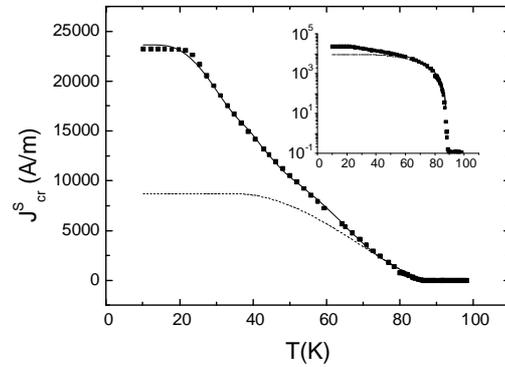
$$3. \quad J_{cr}^S(T) = 2\pi Z k_B T / \phi_0 \delta_o \left(1 - T/T_c\right)^{\frac{3}{2}}.$$

In Eq.(3),  $\delta_o$  is a constant equal to 0.55nm. Eq.(3) is valid above  $T/T_c \approx 0.5$ . For  $T/T_c = 0.5$ ,  $J_{cr}^S(T)$ , as given by Eq.(3), takes its maximum value,  $J_{cr}^S(T)_{max}$ . This suggests that  $J_{cr}^S(T) \approx J_{cr}^S(T)_{max}$  for  $T/T_c < 0.5$  but, as written in the introduction, this is generally not what show the experimental measurements. For this reason, in Ref.[13], it was postulated that the boundary planes include  $n$  stacked groups of  $Z_k$  weak links rows with different critical temperature,  $T_{ck}$  (see Fig.1). For  $T_{c_{j+1}} < T < T_{c_j}$ , this suggestion yields

$$4. \quad J_{cr}^S(T) = \sum_{k=1}^j Z_k J_{crk}^S$$



**Figure 1.** Schematic representation of the postulated  $T_c$  distribution in the boundary planes along the  $c$ -axis of the YBCO films. The dotted lines represent the Josephson weak links rows and the solid lines are the borders of the domains with different  $T_c$ . In this figure we have supposed that the boundary planes include  $n$  domains with different critical temperature  $T_{ck}$  consisting of  $Z_k$  weak links rows.



**Figure 2.** Surface critical current density of film A, whose characteristics are reported in Table 1. The full symbols are computed with Eq.(2) from the magnetic moment measurements and the solid line with Eqs.(4-6) and the data in Table 1. The dotted line shows the contribution of the domain with the highest  $T_c$  ( $T_{c1}=87.8\text{K}$ ) and the inset shows the same curves on a logarithmic scale.

with

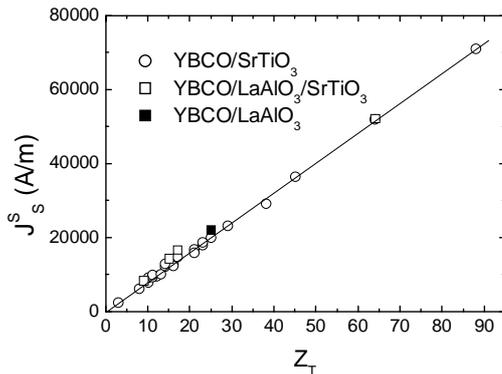
$$5. \quad J_{crk}^S = 2\pi k_B T / \phi_0 \delta_o \left(1 - T/T_{ck}\right)^{\frac{3}{2}} \quad \text{if } T_{ck} > T > 0.5T_{ck}$$

and

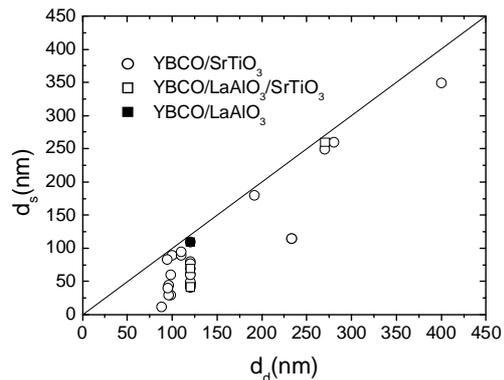
$$6. \quad J_{crk}^S = J_{crkM}^S \quad \text{if } T < 0.5T_{ck}.$$

In Eq.(6),  $J_{crkM}^S$  is the maximum surface critical current density of one row of Josephson weak links in group  $k$ . Fig.2 compares the experimental  $J_{cr}^S(T)$  to the values calculated with Eqs.(46), using the  $T_{ck}$  and  $Z_k$  reported in Table 1. The contribution of the group of weak links rows with the highest  $T_c$  is also reported in Fig.2. Except at very low temperature, there is a very good agreement between the experimental and calculated values.

In order to verify the consistency of the results,  $J_S^S$ , the maximum surface critical current density of the investigated films at low temperature, is reported in Fig.3 as a function of  $Z_T = \sum_{k=1}^n Z_k$ . Fig.3 shows that  $J_S^S$  is proportional to  $Z_T$ . This suggests that the investigated YBCO films have the same



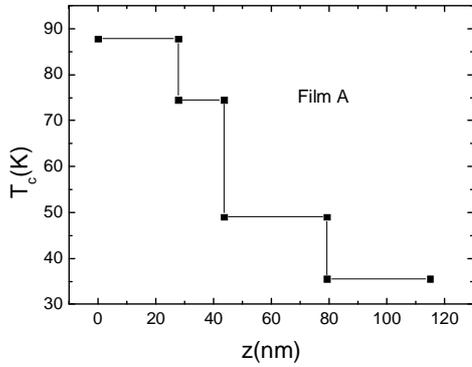
**Figure 3.** Maximum surface critical current density at low temperature of the investigated films,  $J_S^S$ , as a function of the total number,  $Z_T$ , of Josephson weak links rows included in their boundary planes. The symbols correspond to different deposition surfaces. The straight line is a guide for the eye.



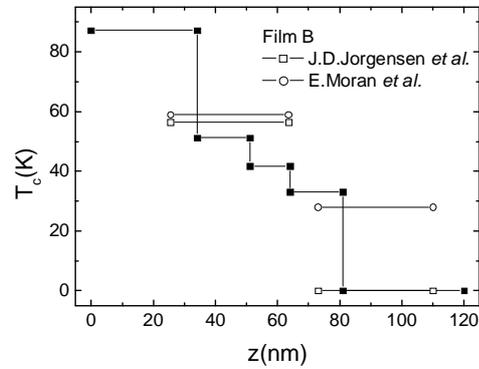
**Figure 4.** Superconducting thickness,  $d_s$ , of the investigated films as a function of  $d_d$ , their physical thickness. The symbols correspond to different deposition surfaces and the straight line to  $d_s = d_d$ .

maximum critical current density,  $j_s$ . This conclusion is consistent with the transport measurements on micro-bridges reported in [11], that yield  $j_s \approx 2 \cdot 10^{11} \text{ A/m}^2$  for all the films. Maximum critical current densities in this range were also reported by other authors [14,15], although larger  $j_s$  were measured on films deposited either on vicinal substrates [14] or on nano-bridges [16, 17]. The superconducting thickness of the films,  $d_s$ , can be determined from  $J_S^S$  and  $j_s$  as  $d_s = J_S^S / j_s$ . Fig.4 shows  $d_s$  as a function of  $d_d$ , the films physical thickness. The solid line in Fig.4 corresponds to  $d_s = d_d$ . While there is a large scattering in  $d_s$  for  $d_d \approx 100\text{-}120\text{nm}$ , the maximum possible value for  $d_s$  is clearly  $d_d$  in the whole range of the investigated thicknesses, that supports the value chosen for  $j_s$  and the validity of the  $d_s$  values.

Annealing experiments in  $^{18}\text{O}$  have suggested that the highest oxygen content and, as a consequence the zone with the highest  $T_c$ , is at the air-film interface [18]. Computing the mean height of the Josephson weak links rows as  $h_m = d_s / \sum_{k=1}^n Z_k$ , it is possible to assign the thickness  $d_k = Z_k h_m$  to domain  $k$  and to plot  $T_c(z)$ , that is the  $T_c$  distribution along the  $c$  axis of the film. This is shown in Fig.5 for film A. It is remarkable that the domain with the highest  $T_c$  is equal to 24% of the film superconducting volume only.



**Figure 5.** Critical temperature as a function of the distance  $z$  to the surface in film A.



**Figure 6.** Comparison of the  $T_c$  profile of film B as obtained from magnetic measurements to the  $T_c$  of the zones investigated by NRERS, as determined from the  $T_c$ -[O] data proposed by i) Jorgensen et al.[20] and ii) Moran et al. [21] for bulk samples.

**Table I.** Substrate, superconducting,  $d_s$ , and deposited thickness,  $d_d$  of films A and B;  $Z_k$  and  $d_k$  are respectively the postulated number of Josephson weak links rows with mean height  $h_m$  and the thickness of the domains with temperature  $T_{ck}$  included in the films.

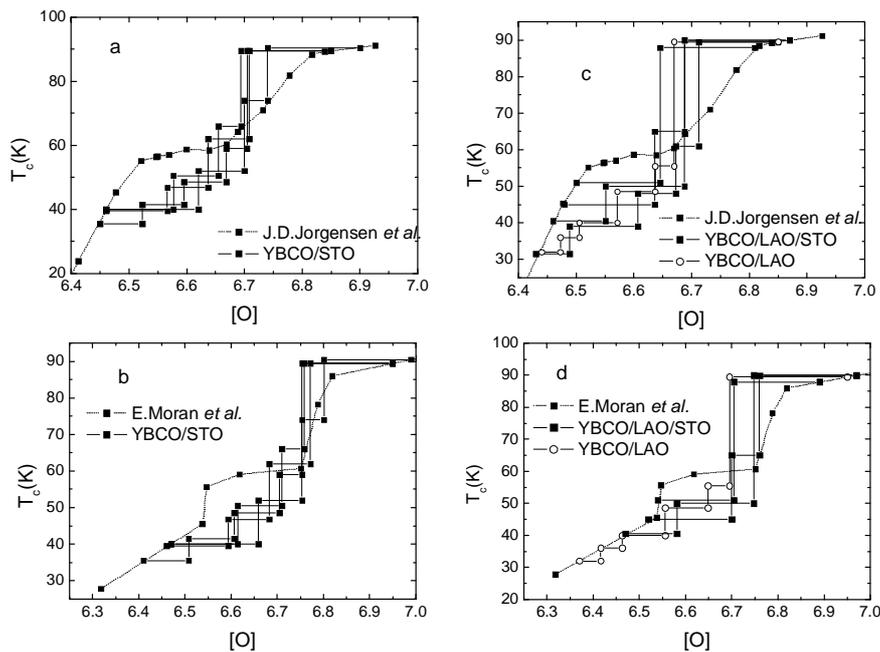
Film	Substrate	$d_s$ (nm)	$d_d$ (nm)	$h_m$ (nm)	$T_{ck}$ (K)	$Z_k$	$d_k$ (nm)
A	SrTiO <sub>3</sub>	115	233	≈ 4	87.8	7	27.8
					74.5	4	15.9
					49	9	35.7
					35.5	9	35.7
B	SrTiO <sub>3</sub>	80	120	≈ 4	87.2	8	34
					51	4	17
					43.5	3	13
					37.5	4	17

In order to confirm the validity of our determination of the  $T_c$  profiles, the oxygen content of film B, whose characteristics are reported in Table 1, was measured by Non Rutherford Elastic Resonance Scattering (NRERS) by J.Siejka (INSP-Paris) [19]. The oxygen content of film B was found to be depth dependent. Using the  $T_c$ -[O] data established for bulk samples by Jorgensen et

al. [20] and by Moran et al. [21] to estimate  $T_c$  in the analysed zones, the obtained  $T_c$  profile is compared to that determined from the magnetic measurements in figure 6. In spite of the uncertainty on the validity of the use for thin films of data established for bulk samples, there is a qualitative agreement between both  $T_c$  profiles.

#### 4. The $T_c$ -[O] relation in the films

During the films fabrication, after the deposition step and the application of the high oxygen pressure in the vacuum chamber, the temperature is decreased at a slow rate. As a result, it is reasonable to assume that the oxygen distribution in the films is near equilibrium and that  $\partial[\text{O}]/\partial t = 0$  after the cooling step. As a consequence of the Fick law, we expect a linear dependence of the films oxygen content on the distance to the surface. Then, the  $[\text{O}](z)$  relation for the superconducting part of a film can be established from the oxygen content at its surface ( $z=0$ ) and at its bottom ( $z=d_s$ ). For this purpose we can take the  $[\text{O}]$  values given by the measurements on bulk samples corresponding to the  $T_c$  determined for  $z=0$  and  $z=d_s$ . From the  $T_c(z)$  and  $[\text{O}](z)$  data we can build the  $T_c$ -[O] graphs. Fig.6 shows the graphs obtained for the films we have investigated, using to determine  $[\text{O}](0)$  and  $[\text{O}](d_s)$ , either the data by Jorgensen et al. [20] (Fig.6a and 6c) or those by Moran et al. [21] (Fig.6b and 6d). Although the  $T_c(z)$  graphs depend on the details of the fabrication process and on the deposition



**Figure 6.** Dependence of the critical temperature  $T_c$  on  $[\text{O}]$ , the oxygen content in YBCO films, calculated from the  $T_c(z)$  yielded by the analysis of the  $J_{\text{cr}}^{\text{S}}(T)$  curves and from the  $T_c$ -[O] data measured on bulk samples i) by Jorgensen et al. [20] (Figs.6a and 6c) and ii) by Moran et al. [21] (Figs.6b and 6d). The  $T_c$ -[O] graphs proposed by these authors are also shown in the figures.

surface, the  $T_c$ -[O] graphs are very similar. They show a first high  $T_c$  step that extends down to  $[\text{O}] = 6.69 \pm 0.05$  for the graphs calculated with the data by Jorgensen et al. and down to

$[O] = 6.74 \pm 0.05$  for the graphs calculated with the data by Moran et al. This step is generally followed by a brutal  $T_c$  decrease down to  $\approx 50K$ . This feature is similar to what is observed above and below  $[O] \approx 6.8$  in bulk samples.

## 5. Discussion and Conclusions

In this work, we have suggested that there is a  $T_c$  gradient in c-axis oriented YBCO films and we have described how the  $T_c$  profiles can be established from magnetic measurements. The validity of this technique is supported by the linear dependence of  $J_S^S$  with  $Z_T$ , that yields a correct estimation of the films superconducting thickness. It is also supported by the comparison between the  $T_c$  profile determined from the magnetic measurements and that established from the results of the NRERS experiment. Assuming that the  $T_c$  gradient is linked to an inhomogeneous oxygen distribution along the c-axis of the films has enabled us to plot  $T_c$ - $[O]$  graphs that are very similar for all the investigated films.

From the applications point of view, it should be possible to increase the critical current in coated conductors for power transportation, by optimizing the length of the plateau with the highest  $T_c$  in the  $T_c(z)$  profile. Preliminary measurements on commercial samples have shown that this plateau extend over  $\approx 50\%$  of the ribbon superconducting thickness.

Otherwise, in high frequency superconducting devices such as antennas, the existence of domains with a critical temperature lower than the working temperature, causes certainly additional losses that hamper their performances. The determination of their  $T_c(z)$  profile should help to optimize the devices by reducing the non-superconducting volume.

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