ARTIFICIAL SUPERCONDUCTING SUPERLATTICES

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In this review are presented the main results of a complex research project devoted to preparation and invesigations of physical properties of [(BaCuO₂)ₙ/(CaCuO₂)ₘ]ₙ artificial superconducting superlattices. The paper starts with the layer-by-layer pulsed laser deposition technique developed for this project and discuss the structure of this new material. The superconducting properties and the effects of structural disorder on them are also presented.

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1. Introduction

All existing high temperature superconducting (HTS) cuprates exhibit a layered structure and can be represented by the general formula \( A_xB_yD_{z}O_{2x+y} \), where A, B and D represent appropriate cations [1], with a stacking sequence [BO - AₓOᵧ - BO] - [[CuO₂]D_{z}]ₙ. The structure of the HTS cuprates is usually considered as made up of two distinct structural subunits having different functions: the [BO - AₓOᵧ - BO] layer, called the charge reservoir (CR) block and the [[CuO₂]D_{z}]ₙ layer, called the infinite layer (IL) block. The CR block can easily include the structure excess oxygen ions or substitutional cations which uncompensate its electrical charge. Some of the excess charge (holes) can be transferred to IL block, giving rise to superconductivity.

Despite many efforts in recent years, the search for new HTS compounds is still based on few simple structural considerations; good superconducting properties (high critical temperature \( T_c \), high irreversibility field \( H_{ir} \) and critical current density \( J_c \) low anisotropy \( \gamma \)) are generally thought to be connected with IL blocks with a low content of structural defects and CR blocks thin and highly metallic.

Quite recently, the use of high pressure synthesis techniques has made possible the discovery of a large number of new metastable HTS cuprates which cannot be synthesized by conventional solid state reaction. Of particular interest among them is the Ba-Ca-Cu-O family [2]. These compounds, with the general formula \( Ca_{m}Ba_{n}Cu_{n}O \), have been reported to have low anisotropy, high \( T_c \) (up to 118 K), high \( J_c \) and \( H_{ir} \) [3]. Such characteristics were attributed to the short spacing between adjacent IL blocks, even shorter than in the case of \( HgBa_2Ca_2Cu_3O_{10} \) and \( TiBa_2Ca_2Cu_3O_7 \). The Ba-Ca-Cu-O system forms a homologous series with \( n \) (number of CuO planes in the IL block) ranging from 3 to 6. The superconducting transition temperature reaches a maximum value (for \( n = 3-4 \)) of 118 K. The chemistry of the CR block for these compounds is quite complicated and not yet fully understood. As an example, it has been shown that Cu sites in the CR block can either be, to a large extent, empty (up to 0.4 vacancies per site) or can contain a large number of substitutional C atoms (up to 0.5 atoms per site) [4]. Recently, it has been shown that the same site can also contain Ca atoms. In this case, the transition temperature increases up to 126 K [5]. Another interesting
feature of these compounds is the high stability of their superconducting properties with respect to the number \( n \) of CuO planes in the IL block (the \( T_c \) of CuBa\(_2\)Ca\(_{n+1}\)Cu\(_n\)O\(_{x+y}\) is the same for \( n = 3 \) and 4) and the chemistry of the CR block (the Cu-1234 and (CuC)-1234 compounds have the same \( T_c \) of 117 - 118 K, and the \( T_c \) of (CaCu)-1223 compound is 126 K).

Considering also the absence of volatile and/or toxic elements apart from the low anisotropy and high \( T_c \), \( J_c \) and \( H_{an} \), these compounds offer very interesting potential applications. Till recently, these materials (due to their high instability) could be obtained in the form of polycrystals or small single crystals only through high pressure synthesis. For future applications involving thin films, different approaches have been made. The first one is the partial substitution of Cu atoms in the CR block with Ti and the use of amorphous phase epitaxy. In this way CuTi-1234 thin films with excellent superconducting properties have been obtained [6]. The second approach is a layer-by-layer “crystallographic engineering”, which is the subject of this review.

2. Layer-by-layer pulsed laser deposition of artificial superconducting superlattices

Recent development in the oxide superlattices (SLs) deposition techniques have opened new perspectives in the field of engineering HTS structures. A large variety of HTS SLs have been grown in the past few years. In most cases superconducting HTS layers of various thickness such as YBa\(_2\)Cu\(_3\)O\(_{x+y}\) or Bi\(_2\)Sr\(_2\)Ca\(_{n+1}\)Cu\(_n\)O\(_{x+y}\) were intercalated with superconducting and non-superconducting layers in order to investigate some fundamental properties of the cuprate superconductors and for future applications. These SLs are commonly named native superconductor superlattices.

A different approach is the growth of new superconducting cuprate artificial structures by not using superconducting individual layers as constituent elements. Instead, the goal is to grow artificial superconducting structures by depositing in sequence IL and CR blocks with specific structural features in order to modulate the superconducting properties of the resulting SL. This new approach in materials science (not only in superconducting materials) can be called crystallographic engineering since, like in genetic engineering, can create something new which does not exist in nature as a stable material. Thin films obtained in this way can be considered either a SL consisting of IL and CR blocks alternately stacked, or a new, artificial, HTS. For this reason they are called artificial superconducting superlattices.

A KrF excimer laser \( \lambda = 248 \) nm with a pulse length of 10 ns and a pulse energy of 225 mJ was used for the PLD growth. In our experimental set-up the laser beam forms an angle of 45° relative to the target surface and the spot beam is focused to 3 mm\(^2\) at the target surface. The targets (1 inch Ba-Cu-O and Ca-Cu-O disks) were mounted on a carousel controlled by a computer. The number of laser shots for each target was varied in order to grow the desired artificial structures. During the deposition, each target rotated around the perpendicular to the surface. No in-situ RHEED diagnostic could be used because of the relatively high oxygen pressure during the growth (0.8-1 mbar). The experimental set-up for the PLD deposition is presented in Fig. 1.

The targets were prepared using the standard solid state reaction technique: stoichiometric mixtures of high purity CaCO\(_3\), BaCO\(_3\) and CuO powders were calcined at 860 °C in air for 24 h, pressed in a disk-shape and finally sintered at 900 °C for 12 h. The pellets obtained in this way were not single phase and had the nominal compositions Ca-Cu-O and, respectively, Ba-Cu\(_{67.5-70}\). The substrates ((100)-oriented SrTiO\(_3\) single-crystals) were placed at a distance of 4.5 cm from the targets on a holder heated at about 600 °C. After deposition the films were quenched to room temperature in few minutes in an argon atmosphere. The structural properties of the films were determined by X-ray diffraction using a 0-2θ Bragg-Brentano diffractometer.
A preliminary step for obtaining artificial superconducting superlattices is the growth of the pure CaCuO$_2$ and BaCuO$_2$ infinite layers. The IL structure is the simplest structure containing the CuO$_2$ planes considered essential for high $T_c$ superconductivity and is constituted by CuO$_2$ planes separated by alkaline earth ions. Such phases are not stable under conventional solid state reaction method and can be obtained by high-pressure (several GPa) synthesis, or in form of thin epitaxial films taking advantage of the pseudomorphic stabilization effect of a suitable substrate. Among the IL phases, by far the least stable is that one containing Ba$^{2+}$ ions. The pure BaCuO$_2$ IL phase can be grown in a very narrow range of growth conditions (substrate temperature, oxygen pressure, etc.) [7], while the CaCuO$_2$ IL phase can be grown in a much wider range of growth conditions, on NdGaO$_2$ substrate. The growth of true IL structures was verified by X-ray diffraction (XRD), high resolution electron microscopy (HREM) and reflection high energy electron diffraction (RHEED). In Fig. 2, the XRD patterns of CaCuO$_2$ (on NdGaO$_3$ substrate) and BaCuO$_2$ (on SrTiO$_3$) infinite layers are presented. The $c$ lattice parameter was calculated from the peak positions and resulted to be 3.2 Å for the CaCuO$_2$ IL and 4.2 Å for the BaCuO$_2$ IL.
Both CaCuO$_2$ and BaCuO$_2$ IL thin films are insulators, with room temperature resistivity higher than 160 Ω·cm. However, a structure consisting of 100 unit cells of CaCuO$_2$ IL grown on top of 32 unit cells of BaCuO$_2$ IL show a semiconductor behavior, with a room temperature resistivity of about 0.4 mΩ·cm and a resistivity at 20 K of about 20 mΩ·cm, as can be seen in Fig. 3. This is a straightforward proof of charge transfer from BaCuO$_2$ layers to CaCuO$_2$ layers.

The next step is the growth of BaCuO$_2$/CaCuO$_2$ superlattices with increasingly thinner modulations. When the thickness of the individual layers is smaller than about 100 Å, superstructure peaks appeared in the X-ray diffraction spectra. Such superstructure peaks were used to precalibrate separately the growth rate of both BaCuO$_2$ and CaCuO$_2$ layers. Once the growth rates were precalibrated, carefully adjusting the number of laser shots for each target on the basis of XRD spectra, (BaCuO$_2$)$_m$/[(CaCuO$_2$)$_n$ superlattices of very good crystallographic quality can be obtained.
with a different number \( m \) of IL layers [8]. These superlattices could be grown at higher temperature and oxygen pressure relative to the BaCuO\(_2\) IL compound. This result suggests that, when a very thin (BaCuO\(_2\))\(_2\) block is stacked in sequence with a (CaCuO\(_2\))\(_2\) block, it can accommodate, relative to the ideal IL structure, excess oxygen ions. Also, it has been observed that good quality SLs cannot be obtained for \( n = 1 \), and that the best quality superlattices are obtained for \( n = 2 \). These facts suggest that (BaCuO\(_2\))\(_2\) consists of an unique stable block rather than two adjacent IL unit cells and give further support that these SLs are closely related to the CuBa\(_2\)Ca\(_{-x}\)CuO\(_2\) compounds obtained by high-pressure technique. A further indication of the modification of the (BaCuO\(_2\))\(_2\) block relative to the pure IL structure is obtained from the measurement of the individual thickness of this block in the superlattice, which resulted to be 8.6 Å (for an oxygen pressure during the growth of 0.8 - 1 mbar), larger than 2×4.2 Å for the pure IL structure. The proposed structure of the (BaCuO\(_2\))\(_2\)/(CaCuO\(_2\))\(_2\) supercell is presented in Fig. 4. It can be seen that, in the IL block, Cu is surrounded by O atoms in planar coordination, while in the CR block, the coordination is pyramidal.

![Diagram](image)

**Fig. 4.** Proposed structure of the (BaCuO\(_2\))\(_2\)/(CaCuO\(_2\))\(_2\) supercell.

However, due to the quite high deposition rate (≈ 2 Å per laser shot) and the discreteness of the PLD process, a perfect structure is quite impossible. Together with the random interfacial roughness, in the case of (BaCuO\(_2\))\(_2\)/(CaCuO\(_2\))\(_2\) SLs appears a coherent interfacial roughness because usually a noninteger number of atomic planes is systematically deposited in each block. Therefore, the crystallographic structure is not commensurate with the chemical cell and, as a result, \( m \) and \( n \) can have noninteger values. A typical XRD spectrum of a HTS SL (with \( T_c = 80 \) K), in the presence of coherent interfacial roughness, is shown in Fig. 5. Peaks are indexed using the standard convention for superlattices. In the case of this SL, the series of satellite peaks of the (001) and (002) average structure peaks do not merge together. From the position of the average structure peaks and of the satellite peaks the “thickness” \( m \) and \( n \) of the individual blocks can be calculated using the following procedure.
Fig. 5. XRD spectrum of a (BaCuO$_2$)$_n$/(CaCuO$_2$)$_m$ superlattice with $T_s = 80$ K (sample A). On the right side is shown the proposed structure. The incommensurability between crystallographic structure and chemical modulation leading to mixed composition interfaces can be noticed.

The period $A$ of our (BaCuO$_2$)$_n$/(CaCuO$_2$)$_m$ superlattice is

$$A = nc_1 + mc_2$$  \hspace{1cm} (1)

where $c_1 (= 4.3 \text{ Å})$ and $c_2 (= 3.2 \text{ Å})$ represent the thickness of a single BaCuO$_2$ layer in the CR block, and of a single CaCuO$_2$ layer in the IL block, respectively, and can be determined from the angular distance between the zero-th order (SL$_0$) peak and the first order satellite peaks (named SL$_{+1}$ and SL$_{-1}$). In fact, knowing the angular position of the zero-th order peak ($\theta_0$), of the first order peaks ($\theta_{\pm1}$) and X-ray wavelength $\lambda$, the superlattice period is given by

$$A = \frac{\lambda}{2|\sin \theta_{\pm1} - \sin \theta_0|}$$  \hspace{1cm} (2)

The average lattice parameter is

$$c = \frac{nc_1 + mc_2}{n + m}$$  \hspace{1cm} (3)

and can be determined from the angular position of the SL$_0$ (001) and/or SL$_0$ (002) peaks in the spectra using the Bragg equation. Finally, the knowledge of $A$, $c$, $c_1$ and $c_2$ allows us to estimate the values of $n$ and $m$ from eqs. (1) and (3). For the superlattice whose XRD spectrum is shown in Fig. 5, $n$ and $m$ are 2 and 2.3, respectively. The proposed crystallographic structure is schematically shown in the same Fig. 5 on the right side of the diffraction spectrum. Mixed composition (Ba$_x$Ca$_{1-x}$)CuO$_2$ layers appear at the interface between the (BaCuO$_2$)$_n$ and (CaCuO$_2$)$_m$ pure layers, with $x$ varying along the growth direction. An example of XRD patterns of (BaCuO$_2$)$_n$/(CaCuO$_2$)$_m$ SLs with $m = 2$, 2.4, 2.7 and 3 is presented in Fig. 6. It can be seen that, for $m = 2$, the second order satellite peaks SL$_{+2}$ (001) and SL$_{-2}$ (002) are superposed, for $m = 2.4$ they are split, for $m = 2.7$ the angular distance between them increases, while for $m = 3$ the angular distance between the peaks obey a simple Bragg law. It can also be noted the change in both peak positions and separations, which obey eqs. (1) - (3).
3. Resistive superconducting transitions and critical temperature

The resistive superconducting transitions $R(T)$, as well as the current-voltage $I-V$ characteristics (discussed in the next chapter) were investigated by the standard four contacts technique. Particular attention was paid to electrical contacts fabrication, since this superlattices are easily damaged by the chemical solvents present in commonly used silver paint. Therefore, the silver pads were painted on the substrates prior to the superlattice deposition, in a configuration that allows an uniform current flow. The superlattices analyzed in this work have a thickness of 400-500 Å, the distance between the voltage contacts of 1-3 mm and the active width of 1-3 mm.

The transport measurements [9] were performed using a Keithley 220 programmable current source and a Keithley 182 sensitive digital voltmeter. The noise level was about 0.5 μV in zero field and a few times higher in applied magnetic fields, up to 1.2 T. The $R(T,B)$ measurements were performed with a transport current of 30 μA and at a cooling (heating) controlled rate of 1-2 K/min. As an example, in Fig. 7 is presented (in both linear and logarithmic scales) the resistive transition of a $\text{(BaCuO}_2\text{)}_2/\text{(CaCuO}_2\text{)}_{23}$ superlattice whose XRD pattern is presented in Fig. 5.

![Fig. 6. XRD patterns of (BaCuO$_2$)$_2$/CaCuO$_2$)$_m$ SLs with $m = 2, 2.4, 2.7$ and 3.](image)

![Fig. 7. Temperature dependence of resistivity for the same SL as in Fig. 5 (sample A). Inset: superconducting transition in logarithmic scale.](image)
The particular features of the \( R(T) \) curves will be discussed later. In this chapter we will analyze only the dependence of the critical temperature on various parameters. Apart from the desired artificial structure, the critical temperature depends on the targets composition and morphology, oxygen pressure and substrate temperature during growth. The highest \( T_c \) (of 81 K at zero resistance) was obtained for non-stoichiometric Ca-Cu-O target. The use of stoichiometric target decreased the highest critical temperature with about 8 K. Regarding the oxygen pressure, the range for best results is quite high, namely 0.7 - 1.2 mbar, with the condition that the pressure is stable during growth. The growth parameter which has the most significant influence on \( T_c \) is the substrate temperature during growth \( T_s \). Since we measured \( T_s \) with a thermocouple inserted in the substrate holder, the actual substrate temperature may be different than the nominal \( T_s \), therefore the absolute values of \( T_s \) may be irrelevant. In the following, we will discuss the dependence of \( T_c \) on the growth temperature relative to the growth temperature which resulted in the highest critical temperature, namely \( T_c^{\text{CR}} \). In Fig. 8, the resistive transitions of several (BaCuO\(_2\))/(CaCuO\(_2\))\(_m\) SLs, with \( m = 2 \), grown at different \( T_s \) are presented. Curves 1 to 6 correspond to the following growing temperatures, respectively: \( T_s^{\text{CR}} \), \( T_s^{\text{CR}} - 10 \), \( T_s^{\text{CR}} - 20 \), \( T_s^{\text{CR}} - 30 \), \( T_s^{\text{CR}} - 40 \), and \( T_s^{\text{CR}} - 50 \). In this set of depositions, the nominal \( T_s^{\text{CR}} \) was 640 °C.

\[ T_s^{\text{CR}} - 20 \]

![Graph](image)

**Fig. 8.** Temperature dependence of resistivity for (BaCuO\(_2\))/(CaCuO\(_2\))\(_m\) SLs grown at various \( T_s \): from 1 to 6: \( T_s^{\text{CR}} \), \( T_s^{\text{CR}} - 10 \), \( T_s^{\text{CR}} - 20 \), \( T_s^{\text{CR}} - 30 \), \( T_s^{\text{CR}} - 40 \), and \( T_s^{\text{CR}} - 50 \).

It can be seen that \( T_c \), normal state resistivity and the shape of the \( R(T) \) curves strongly depend on the growth temperature. It is worth noting that a further increase of \( T_s \) resulted in the decomposition of the artificial superconducting superlattice.

We have also studied the dependence of the critical temperature on the thickness of the film, i.e. the number \( N \) of unit cells of the \( [(\text{BaCuO}_2)/\text{(CaCuO}_2)]_2 \) artificial superconducting superlattices. The majority of the SLs we have grown had \( N \) between 25 and 35. However, in order to determine the influence of the film thickness on the superconducting properties, we have also grown SLs with 4, 8, 15 and 100 unit cells. The dependence of the critical temperature on the number of unit cells \( N \) is presented in Fig. 9. It can be seen that, for \( N \) between 8 and 100, \( T_c \) variation is within the normal statistical spreading, while for SLs with 4 unit cells, the critical temperature drops to about 20 K. In our opinion, this is due to the presence, in the first few unit cells, of significant random interfacial roughness which arise from substrate roughness, growth rate fluctuations, island growth mode, interdiffusion, etc. In other words, the first 4-5 unit cells are of poor quality. A further confirmation of this fact is the nominal normal state resistivity of the 8-unit cells superlattice, which is more than double that of SLs with \( N = 15-35 \), despite the high value of \( T_c \) (about 70 K). Also, from the nominal normal state resistivity of the thickest superlattice (\( N = 100 \)), also much higher than that of SLs with \( N = 15-35 \), we have found that the stabilization effect of the substrate disappears after about 50 unit cells.
More interesting is the dependence of the critical temperature on the number \( m \) of CaCuO\(_2\) layers in the \((\text{BaCuO}_2)_y/(\text{CaCuO}_2)_z\)\(_{10}\) superlattices with 25-35 unit cells [10,11] grown in the same conditions, presented in the inset of Fig. 9. No difference can be noticed between the commensurate (integer \( m \)) and the incommensurate (noninteger \( m \)) structures: within the experimental error and statistical spread all the \( T_c \) values lie on the same curve.

![Fig. 9. Dependence of the critical temperature on the number \( N \) of unit cells of \((\text{BaCuO}_2)_y/(\text{CaCuO}_2)_z\)\(_{10}\) SLs. Inset: dependence of \( T_c \) on the number \( m \) of CaCuO\(_2\) layers.](image)

From the inset of Fig. 9 it can be seen that the behavior of \( T_c \) versus \( m \) indeed follows qualitatively the expected dependence with a maximum \( T_c \) occurring for \( m \) between 2 and 3 (which corresponds to 3-4 CuO\(_2\) planes in the IL block). Moreover, the decrease of \( T_c \) with increasing \( m \), for \( m \geq 3 \) (underdoped region), can be explained qualitatively by taking into account the decrease of the carriers concentration per CuO\(_2\) plane \( c_o \): in the inset of Fig. 9 the dot line indicates the \( T_c \propto 1/m \) behavior (\( T_c \) was supposed to decrease linearly with \( c_o \) and to reach zero for \( c_o \equiv 0.06 \) holes per CuO\(_2\) plane). The maximum value of \( T_c \) (about 80 K) was lower than expected (for a cuprate containing 3-4 CuO\(_2\) planes and an optimum carrier concentration, \( T_c \) should be above 100 K). Furthermore, the behavior of \( R(T) \) for SLs having the thinnest IL block \( (m = 1) \) was non-metallic despite of the highest carrier concentration. All these features were explained considering the high degree of disorder in these artificial structures [11] and will be address in the last chapter of this review.

4. \( I-V \) curves and critical current density

The \( I-V \) characteristics were measured with double-polarity square current pulses of 0.1 sec width, from 1 \( \mu \text{A} \) to 100 mA, with the period between successive acquisitions increasing quadratically with current, in order to allow the Joule heat to be absorbed by the copper holder. The temperature was stabilized within 20 mK during each \( I-V \) measurement, with increasing and decreasing current and no hysteresis was detected between the two branches of the \( I-V \) curves, in the experimental window discussed in the review. In Fig. 10, the \( I-V \) characteristics in zero applied magnetic field of the same SL, for temperatures between 62 and 82 K, are presented in a double-logarithmic plot. The difference in temperature between two curves is about 1 K at high temperatures, about 0.5 K in the vicinity of the curvature change, about 1 K and about 2 K at low temperatures. It can be seen that, for \( T \) smaller than 77.5 K, the \( I-V \) curves have a downward curvature, in our
experimental window. This feature can be explained in the frame of the Jensen-Minnhagen (JM) theory of current-induced unbinding of thermally-created vortex-antivortex pairs, taking into account the Josephson coupling between adjacent superconducting planes [12], which predicts the existence of a finite critical (unbinding) current $I_{c2}$ decreasing linearly with increasing temperature (but not close to $T_c$) and non-linear $I$-$V$ curves for $I > I_{c1}$ of the form:

$$V \propto (I - I_{c1})^{\alpha - 1}$$  \hspace{1cm} (4)

with $\alpha$ the JM exponent, which, for $I >> I_{c1}$, reduces to the two-dimensional (2D) Kosterlitz-Thouless-type power-law.

![Fig. 10. Current-voltage characteristics of the sample A in zero applied magnetic field. The full lines represent attempted three parameter fit with the Jensen-Minnhagen model (Eq. (4)).](image)

In Fig. 10, the full lines represent attempted three-parameter fits with Eq. (4), transformed for the $\log(V)$ scale. As can be seen, the experimental $I$-$V$ curves are well described by the model even in the case of our artificial structures with intrinsic high disorder.

In Fig. 11 are reported the $I$-$V$ characteristics measurements in applied magnetic fields perpendicular to $(a,b)$-planes: a) $B = 0.55$ kGs for $T$ between 57 and 79.8 K; b) $B = 4.4$ kGs for $T$ between 55.8 and 78.1 K; and c) $B = 10.8$ kGs for $T$ between 49.7 and 75.4 K.

![Fig. 11. $I$-$V$ curves of sample A in three magnetic fields. The dashed lines represent power-law fits at the chosen melting temperatures.](image)
These $I$-$V$ curves apparently display the common transition between a vortex-glass (VG) and a vortex liquid (VL) [13], at a melting temperature $T_m(B)$, indicated as a straight dashed line in the figures. Above $T_m(B)$ the $I$-$V$ curves crossover from an Ohmic behavior at low currents to a power law relation at high currents and every $I$-$V$ curve displays an upward curvature. Below $T_m(B)$ the $I$-$V$ curves show an exponential relation at low currents and a power-law behavior at high currents, with a downward curvature, suggesting that the system approaches to a truly superconducting phase (VG) for $I$ exponentially small. At $T_m(B)$, where is the crossover between downward and upward curvatures, the whole $I$-$V$ curve displays a power law relation which takes the form

$$V(I, T = T_m) \propto I^{(d+1)/(d-1)},$$

where $\varepsilon$ is a critical exponent (dynamic exponent) of VG and $d$ is the dimensionality. The melting temperatures in the three applied magnetic fields (0.55, 4.4 and 10.8 kGs) are 72.8, 70.9 and 68.1 K, respectively. Since $I$-$V$ curves were measured at an interval of about 1 K around $T_m(B)$, the uncertainty of melting temperature was ±1 K.

The dynamic exponent $\varepsilon$ was determined from Eq. (5), taking the slope of the $I$-$V$ curves at $T_m(B)$ fitted with the power-law, and $d = 3$. To establish the uncertainty in $\varepsilon$, we applied the same procedure on the curves adjacent to the $I$-$V$ curve at $T_m(B)$. In this way, we determined the dynamic exponent, for each field, to be 4.3, 3.8 and 3.1, respectively, with an uncertainty of ±0.3. On the other hand, above $T_m(B)$ and for low currents (the ohmic region in the $I$-$V$ curves), the linear resistance $R(T)$ can be scaled as

$$R(T) \propto (T/T_m - 1)^{(\varepsilon + 2 - d)}$$

where $\nu$ is the static critical exponent. By fitting Eq. (6) on the experimental data for $B = 0.55$ kGs and considering $d = 3$, $\nu$ is determined to be 2±0.3.

From the common analysis procedure, i.e., according to the scaling function [13]

$$\frac{V}{I^{(d+1)/(d-1)}} = F_{\varepsilon} \left[ \frac{I}{T^{(d+1)/(d-1)}} \right]$$

the $I$-$V$ curves shown in Fig. 11 can be collapsed onto a single scaling curve with two branches, for $T > T_m(B)$ and for $T < T_m(B)$, respectively. This procedure was performed by plotting, for each field, the $I$-$V$ curves as $\log_{10}(V/I^{d+1})$ vs $\log_{10}(I/T_m^{d+1})$. The scaling collapses of the $I$-$V$ curves for the three values of applied magnetic field are presented in Fig. 12. It is worth noting that we did not try to adjust $T_m$ or $\nu$ (determined as discussed above) in order to obtain a better scaling collapse and we implied a value 2 for the static exponent for all three fields. Therefore, these scaling collapses can quite directly reflect the experimental facts.

The values of the critical exponents are not far from the typical values for 3D VG transitions: $\varepsilon \sim 4 - 6$ and $\nu \sim 1 - 2$ [13]. A somehow lower value of our dynamic critical exponent could be explained by an anisotropy factor larger than in the case of YBa$_2$Cu$_3$O$_7$ (as we shall discuss later on in the paper). Dynamic exponents $\varepsilon = 2.4 ± 0.6$ were obtained in the case of more anisotropic Tl$_2$Ba$_2$Ca$_2$Cu$_3$O$_{10}$, for fields up to 2 kGs, while for larger fields a 3D-2D dimensional crossover was observed [14].
Fig. 12. The scaling collapse of I-V curves of sample A, using the same static critical exponent $\nu=2$ and the dynamic critical exponents obtained from the slopes of the dashed lines in Fig. 11.

From the experimental current-voltage characteristics we estimated also the critical current density $J_c$ at a dissipation criterion of 5 $\mu$V/cm, which was our noise level for the measurements in fields lower than 5 kGs. In Fig. 13, the $J_c(T)$ dependence in zero field and in $B=4.4$ kGs is presented.

Fig. 13. Temperature dependence of the critical current density of sample A in zero field and in 4.4 kG at a voltage criterion of 5 $\mu$V/cm.

Again, the uncertainty upon the absolute values due to geometric factors was estimated at about 20%. Linear extrapolation to $T=0$ (taking only the low-temperature points, where the temperature dependence of $J_c$ seems linear) gives a value for $J_c(0) \sim 8 \times 10^7$ A/cm$^2$ for $B=0$, and about half of this value in 4.4 kGs. These estimations are consistent with the value reported in Ref.15 from magnetization measurements ($J_c(T=10\text{ K}) \sim 6 \times 10^7$ A/cm$^2$) on a sample with the same structural properties but with $T_c=74\text{ K}$. 
5. Vortex-liquid phase and anisotropy

In order to study the dissipation in the vortex-liquid (VL) phase, we measured the resistive transitions in field-cooling conditions in magnetic fields between 0.2 and 9.8 kGs, perpendicular to \((a,b)\)-planes. In the case of later field, the decrease in \(T_c\) (zero-resistivity in the limit of the noise in our measurements) is between 8-10 K, depending on the sample. In Fig. 14 such transitions are shown in Arrhenius plots for sample A.

![Arrhenius plots](image)

Fig. 14. Arrhenius plots of the resistance of sample A in the following applied magnetic fields:

- 0.21, 0.34, 0.55, 0.86, 1.43, 2.27, 3.33, 4.39, 5.44, 6.48, 7.49, 8.45, 9.21 and 9.81 kG.

It can be noticed a significant curvature in Arrhenius plots which are clearly not straight lines over more than one order of magnitude in resistance. This behavior was recently reported also in Tl2Ba2CaCu2O8 films [16] and in Bi2Sr2CaCu2O8 films in low magnetic fields [17] and was explained either by considering that the transition into VG state is cut off at some length scale [16], or by an increased viscosity of the VL with a deformation time longer than the pinning time, due to high energy barriers associated with the thermally activated plastic motion of vortex system [17].

Since in our samples there is an important quenched disorder due to SL imperfections, we believe that the later explanation could be valid in the case of our measurements. At low transport currents (30 \(\mu\)A for these measurements) and at low levels of dissipation, a thermally assisted flux flow is expected to be the mechanism of dissipation. In this case, the resistance is given by:

\[
R(T,B) = R_0 e^{\frac{U(T,B)}{T}}
\]

(8)

where \(U(T,B)\) is the activation energy (with the Boltzmann constant \(k_B = 1\)).

One can determine the activation energy \(U(T)\) directly, from the resistive transitions for constant \(B\), using Eq. (8) and making the natural assumption that \(U(T)\) vanishes at the mean-field critical temperature \(T_{\alpha}\): \(U(T) = T_\alpha \ln[R(T_{\alpha})] - \ln[R(T)]\). For the discussed data, the mean-field critical temperature was approximated by the temperature value corresponding to the inflection point in the \(R(T)\) dependence, \(T_{\alpha} = 83\) K, which was approximately the same for all fields in our experiment. In Fig. 9, the activation energy determined this way is presented, for three magnetic fields: 0.38, 3.33 and 9.21 kGs, respectively.
Fig. 15. Temperature dependence of the activation energy $U$ of sample $A$, at three magnetic fields. The dot lines represent linear fits of the low dissipation regions. Inset: magnetic field dependence of the activation energy $U_0$, in a double-logarithmic plot. The full line represents the power-law fit in low fields regions ($U_0 \propto B^{-0.135}$), while the dot line represents the $U_0 \propto B^{-1.02}$ dependence.

As can be seen, for a limited resistivity interval, at low resistivity levels (in the sensitivity window of our measurements), the $U(B,T)$ dependence can be considered of the form $U(B,T) = U_0(B)(1 - T/T')$, with $T' \ll T_0$ (the dashed lines in Fig. 15).

Similar linear fit was performed on all $U(T)$ curves at low resistivity levels, resulting $U_0(B)$ and $T'(B)$ as fitting parameters. The inset to Fig. 15 shows, in a double logarithmic plot, the field dependence of $U_0$. One can see that, at fields up to about 5 KGs, the activation energy varies slowly with $B$, as expected close to the isolated vortex limit in the presence of quenched disorder. The fit in the low fields region gives in fact a field dependence of the form $U_0 \propto B^{-0.135}$. For higher fields, the activation energy seems to be proportional to $B^{-1.02}$, which is characteristic for cutting and reconnection of vortices that appear in the case of thermally activated plastic motion of an entangled vortex liquid [17]. It is important to notice that even in fields higher than 5 KGs where $U_0 \propto B^{-1.02}$, the Arrhenius plots are not straight lines over more than one order of magnitude, and $T'$ does not approach $T_0$ in the $U(T)$ plots, as was the case of the Bi$_2$Sr$_2$CaCu$_2$O$_8$ films analyzed in Ref. 17. This is probably due to the broad transitions (even in zero field) in the case of our superlattices.

One of the most important parameter that characterize any HTSC material is the anisotropy factor $\gamma = (m^*_m/m^*_y)^{1/2}$, where $m^*_m$ and $m^*_y$ are the effective masses of Cooper pairs perpendicular and, respectively, parallel to the superconducting $(a,b)$-planes. Since a direct measurement of the anisotropy factor seems extremely difficult in the special case of our artificially layered SL, we tried an indirect way of estimating $\gamma$ through the study of the melting line which separates VG and VL phases in the vortex phase diagram.

As was shown by Tinkham [18], analysis of the melting transition in the frame of Blatter et al. rescaling approach [19] gives the following dependence of the melting field $B_m$ on temperature and on field orientation in respect to the $(a,b)$-planes:

$$B_m = \frac{C_4 \Phi_0^2}{(k_B T)^3 \lambda_0^4 \gamma (\cos^2 \alpha + \gamma^2 \sin^2 \alpha)^{-1/2}} \quad (9)$$
where $C$ is a constant ($C = 1/4\pi^2$), $c_i$ is the empirical Lindemann parameter, $\Phi_0$ is the magnetic flux quanta, $\lambda_{\text{coh}}$ is the penetration depth along the $(a,b)$-plane, and $\alpha$ is the angle between the magnetic field lines and the $(a,b)$-planes. By using the “two-fluid” temperature dependence of the coherence length $\lambda_{\text{coh}}(T) = \lambda_{\text{coh}}(0) \left[1-(T/T_c)\right]^{1/2}$, from Eq. (9) one can obtain the explicit $T$ and $\alpha$ dependence of the melting field, which is anisotropy-dependent.

In the first case, the resistive transitions in different applied fields, perpendicular to the $(a,b)$-planes ($\alpha = 90^\circ$) were used. For every field, we determined the temperature where the on-set of dissipation occurs (in the limit of our resolution, which was $B/R(100 \text{ K}) \approx 10^3$) which was considered as the melting temperature (i.e., for $T = T_c$, the applied magnetic field becomes $B_m$). In Fig. 16, the dependence of $B_m$ on the reduced temperature $T/T_c$ is presented, for three different samples. The full lines represent fits with the equation (9), modified to take into account the $\lambda_{\text{coh}}(T)$ dependence and the $\alpha = 90^\circ$ value. From the fitting parameter, taking $c_i = 0.15$ and $\lambda_{\text{coh}}(0) = 1500 \text{ Å}$, which are typical values for HTSC [22], the values of the anisotropy factor $\gamma$ are estimated for the three samples, namely 17.8, 20.4 and 25, respectively.

![Fig. 16. Dependence of the melting field $B_m$ on the reduced temperature $T/T_c$ for samples A (circle), B (square) and C (triangle). The full lines represent the fit with Eq. (9) for perpendicular field. The resulting values for $\gamma$ are 17.8, 25 and 20.4, respectively.](image)

Of course, the absolute values of the anisotropy factor are only estimations, subject to errors due to the uncertainty in choosing the right Lindemann parameter and to our experimental resolution, but the relative differences between $\gamma$ for the three samples are objective facts, most probably due to slightly different effective thickness of the CR block. However, if we compare the reduced temperature for which $B_m = 10 \text{ kG}$ in YBa$_2$Cu$_3$O$_y$ ($T/T_c \approx 0.95$), in Bi$_2$Sr$_2$CaCu$_2$O$_y$ ($T/T_c \approx 0.4 - 0.5$) from literature (for example [18]), with $T/T_c \approx 0.85 - 0.9$ for our samples, an anisotropy factor of about 20 seems reasonable, compared with the well-known values of about 7 for YBa$_2$Cu$_3$O$_y$ and 150 for Bi$_2$Sr$_2$CaCu$_2$O$_y$.

The second set of measurements concerning the estimation of $\gamma$ was performed at constant temperature (within 20 mK) and different field orientations ($c_i$), with the magnetic flux lines always perpendicular on the transport current. At a given angle, the magnetic field was increased till a dissipation twice the noise level was observed, and that field was taken as $B_m$. As we noticed, the dissipation raised extremely fast with small increment of the field, therefore, our chosen criterion does not involve a significant error in determining the $B_m(\alpha)$ dependence. Such dependence is shown in Fig. 17, for two samples at the reduced temperatures 0.991 and 0.988, respectively, high enough to insure a coherence length along the c-axis larger than the interlayer spacing, in which case the anisotropic 3D approach leading to Eq. (9) is appropriate. Since it was shown [20] that for angles $\alpha < 1^\circ$ the flux lines are “locked in” between the layers due to the strong intrinsic pinning by the layered structure itself [21], we restrained the analysis of the $B_m(\alpha)$ dependence only to $\alpha > 1^\circ$ experimental values.
Fig. 17. Dependence of the melting field on the angle between the field lines and (a,b)-planes, for samples B and C at constant temperatures. The full lines represent the fit with Eq. (9) for $T = \text{ct}$.

In fact, for smaller angles, a very sharp peak was observed (not shown in the figure). Again, the data were fitted (full lines in Fig. 17) with Eq. (9) rewritten for constant temperature. In this case, the anisotropy $\gamma$ is itself a fitting parameter, independent on estimations of $c_L$ and $\lambda(0)$, and resulted to be about 20 and 22 for the two samples, respectively, values surprisingly similar to those obtained from the $B_m(T)$ dependence.

6. Effects of structural disorder on the transport properties

The behavior of the normal state resistivity versus temperature of our artificial HTS structures for $m = 2$, grown under optimized conditions, shows a number of unusual but reproducible features [22] which can be clearly seen in Fig. 18: (a) a quite high value of the resistivity at room temperature [$\rho(300 \text{ K}) \approx 800 \mu\Omega\text{cm}$]; (b) a negative curvature of the $\rho(T)$ experimental curve with no trace (up to 350 K) of the linear normal state behavior typical of the HTS materials; (c) a pronounced rounding at the $\rho(T)$ behavior well above the temperature of zero resistance with a sizable broadening of the transition itself (about 15 K, using the 10% - 90% criterion). We believe that the transport properties are related to the special role of structural disorder in such artificial structures.

The first consequence of the high degree of disorder is the decrease of the mean free path $l$ with respect to the ordered structures. This effect results in a noticeable increase of the residual normal state electrical resistivity $\rho_0$ relative to values usually measured for good quality HTS films. However, already for good quality HTS films, $l \approx 20-100 \text{ Å}$, therefore a further decrease of the mean free path would lead the system close to the localization transition ($l \approx a$, where $a$ represents the in-plane lattice parameter). In these conditions the behavior of $\rho$ versus temperature is no longer represented by a simple linear law [23].
Fig. 18. Behavior of resistivity vs. temperature for sample A. The full line represents the fit with the shunt resistor model. Inset: $T_c$ vs. residual resistivity for various (BaCuO$_2$)$_2$(CaCuO$_2$)$_2$ SLs grown under different conditions (except the oxygen pressure kept at the optimum value of about 1 mbar).

In particular, it has been shown that the electrical resistivity saturates at high temperature at a characteristic resistivity of the same order of magnitude as the Mott maximum metallic resistivity $\rho_{\text{max}}$. Numerical values of the maximum resistivity depend on the specific system; however, in the case of a 2D system the “resistivity per square area” has universal value $R_x^{\text{max}} = h/e^2 \approx 26 \, \Omega$, where $h$ is the Planck constant and $e$ is the electron charge. A model which fits the data on saturation quite well is that of a shunt resistor $\rho_s$ in parallel to the actual system. In this case one has [24,25]

$$
\frac{1}{\rho(T)} = \frac{1}{\rho_0} + \frac{1}{\rho_s(T)} + \frac{1}{\rho_s}
$$

where $\rho_0$ is the residual resistivity and $\rho_s$ represents the linear contribution. Our experimental data have been fitted with Eq. (10) in the temperature range between 180 K and 350 K assuming a linear behavior of $\rho_s(T)$ in accordance with the usual properties of the HTS materials. The result of the fit for sample A is shown in Fig. 18 by the full line. The agreement with the experimental data is very good between room temperature and 140 K. Below this value thermodynamic fluctuations cause a sizable difference between the fit and the experimental data. From the fit a reproducible $\rho_s$ value of about 2 m$\\Omega$cm is obtained. The value of $R_x^{\text{max}}$, calculated dividing the $\rho_s$ value by the thickness $d$ of an individual IL (CaCuO$_2$)$_2$ block (6.4 Å) is 30 $\Omega$, in surprisingly good agreement with the maximum value of $R_x^{\text{max}}$ obtained according to the Mott argument in the two-dimensional case (26 $\Omega$). The value of the residual resistivity $\rho_0$ of superlattices, grown in optimal conditions, is about 200 $\mu$Omega cm. An estimate of the parameter $\varepsilon$ obtained in a simple Drude model from the residual resistivity gives a value of 3-4 $h$.

Another important effect of disorder is the decrease of $T_c$ with respect to the one of the thermodynamically stable HTS materials with 3-4 CuO$_2$ layers in the IL block, which have critical temperatures higher than 100 K. As was shown in Fig. 9, the highest $T_c$ achieved for our SLs is about 80 K. However, such a reduction of the critical temperature is a characteristic feature in native superconducting superlattices and in disordered HTS systems such those obtained by impurity doping in the IL block or radiation damage. In the analysis of our data we followed the theoretical approach to the problem of the superconducting transition in highly disordered films by Finkel'shtein [26]. That is, starting from the experimental value of $R_x^{\text{max}}$ estimated for $T \to 0$, and assuming a decrease of the transition temperature, relative to the $T_c$ of the natural HTS
compounds of about 20% \((T_d/T_c) = 0.8\), a value of \(\phi_T \approx 3h\) was estimated, in excellent agreement with that estimated from the residual resistivity. A further support to the scenario outlined above is given by the data reported in the inset of Fig. 18, where \(T_c\) (zero resistance) is presented as function of residual resistivity, for a number of \((\text{BaCuO}_2)_{12}/(\text{CaCuO}_2)_{2}\) superlattices grown at the same oxygen pressure but varying the growth temperature, the target thermal treatments, the laser fluence and focialization, on the way to find the optimum growth conditions. A clear inverse correlation is seen between \(\rho_0\) and \(T_c\) with a value of \(T_c\) extrapolated at zero residual resistivity (negligible structural disorder) of about 100 K.

Another important aspect is the effect of fluctuations on the shape of the superconducting transition. We neglect, as is usually done for the in-plane resistivity in HTS materials, both the density-of-states (DOS) and Maki-Thompson contribution, taking into account only the Aslamazov-Larkin (AL) fluctuations. Two-dimensional disordered systems represent an ideal sample for the study of paraconductivity: in this case the role of fluctuations is strongly enhanced by disorder. Indeed the AL contribution to conductivity does not contain any characteristic of the material except the effective thickness \(d\) and the critical temperature, while the normal state conductivity, affected by disorder, is considerably lower relative to standard HTS materials. This result in a strong enhancement of the relative role of fluctuations. A simple estimate of the related broadening of the transition can be easily obtained calculating the temperature value for which the AL conductivity \(\Delta \sigma_{AL}\) is already \(\sigma_n/\epsilon\), where \(\sigma_n\) is the normal state resistivity and \(\epsilon\) is the Euler base of the natural logarithm. In a Drude Model this value can be estimated in the following way:

\[
\frac{\Delta \sigma_{AL}}{\sigma_n} = \frac{\pi}{16} \frac{h}{\phi_T \tau} \epsilon^{-1}
\]

where \(\epsilon = \ln(T/T_c)\), \(\tau\) is the electronic relaxation time, and \(\phi_T\) is the Fermi energy. Assuming a value of \(\phi_T \tau/h \approx 3\), as deduced from the previous arguments, and \(\Delta \sigma_{AL}/\sigma_n = 1/2.73 \approx 0.3\), we obtain \(\epsilon \approx \pi/16\), which corresponds to a broadening of the transition of about 15 K, namely, very close to the observed value. Under these conditions the regime of critical fluctuations extends well beyond the usual temperature range up to about 100 K. Therefore, the standard approach for the calculation of paraconductivity can be applied only outside of this temperature range, namely, for \(\ln(\epsilon) \gtrsim -1.5\). In such a temperature range, however, the AL approach must be extended taking into account also the short wavelength fluctuations which predicts a universal temperature dependence of paraconductivity, well above the superconducting transition, of the form \(\Delta \sigma_\parallel \propto \epsilon^{-3}\) [27]. In Fig. 19 the behavior of \(\Delta \sigma_\parallel\) for two SLs with the same transition temperature is shown in a double-logarithmic plot. It can be seen that, for \(\ln(\epsilon) \gtrsim -1.5\), \(\ln(\Delta \sigma_\parallel)\) vs. \(\ln(\epsilon)\) follows, as expected, a linear law with a slope of -3.

It is quite impressive the fact that the normal state resistivity behavior, enhanced thermodynamic fluctuations and decrease of the critical temperature can be explained by the effect of the structural disorder, in the frame of various theoretical models, with a single numerical value of the localization parameter \(\phi_T \tau/h \approx 3\).
Fig. 19. Normalized excess conductivity $r(\varepsilon) = (16\hbar e^2/\pi^2)\Delta\sigma_0$ vs. $\varepsilon = \ln(T/T_c)$ in a ln-ln scale for two different samples having $T_c \approx 80$ K. The vertical dot line indicates the temperature for which $\Delta\sigma_0/\sigma_0 \approx 0.3$. The solid line represents the extended theory by Reggiani et al. (Ref. 27) applied in the temperature region above $\ln(\varepsilon) \geq -1.5$.

7. Conclusions

Layer-by-layer Pulsed Laser Deposition is a very promising technique for crystallographic engineering of artificial metastable structures by using the pseudomorphic stabilization effect of various substrates. Even if our review presents the results on artificial superconducting superlattices, the above-mentioned technique can be also used for other various materials, with different physical properties and future potential applications.

By varying the number of laser shots on each of the two targets, we were able to fabricate various $[(\text{BaCuO}_2)_n/(\text{CaCuO}_2)_m]_N$ superconducting superlattices, consisting of IL blocks alternately stacked with CR blocks. Good crystallographic properties were obtained for $n = 2$, while the best superconducting properties were achieved for $n = 2$ and $m$ between 2 and 2.5. We also found that the first 4-5 unit cells are of poor quality due to the interfacial disorder, and the stabilization effect of the substrate is lost after about 50 unit cells.

The superconducting properties (current-voltage characteristics, properties of the vortex liquid phase, melting line, etc.) are qualitatively similar to native HTS materials. Both anisotropy and critical current density are between Y-based and Bi-based superconductors. The unusual features of the resistive transitions and the effect of thermal fluctuations were successfully explained by the high degree of coherent disorder, using a single numerical value of the localization parameter.

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