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Citation

Yang, Z. -Q., Hendrikx, R. W. A., Aarts, J., Qin, Y., & Zandbergen, H. W. (2003). Strain release of (La,Ca)MnO₃ thin films by Yba₂Cu₃O_{7-δ}. *Physical Review B : Condensed Matter*, 67, 024408. doi:10.1103/PhysRevB.67.024408

Version: Not Applicable (or Unknown)

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Note: To cite this publication please use the final published version (if applicable).

Strain release of (La,Ca)MnO₃ thin films by YBa₂Cu₃O_{7- δ}

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(Received 11 December 2001; revised manuscript received 21 March 2002; published 13 January 2003)

La_{1-x}Ca_xMnO₃ ($x \approx 0.3$; LCMO) films of different thickness were sputter deposited on single-crystal substrates of SrTiO₃(100) and LaAlO₃(100) with and without YBa₂Cu₃O_{7- δ} (YBCO) as template layer, in order to study the effects of substrate strain and strain release on the physical properties and the microstructure of the films. Clear differences in the lattice parameters and the temperature of the metal-insulator transition, as well as comparison with films grown on a lattice-matched substrate [NdGaO₃(110)] show that the YBCO buffer layer is very effective in relaxing the strain of the LCMO films, which is quite difficult to release in LCMO films directly deposited on SrTiO₃. The template is also very effective in promoting growth on LaAlO₃.

DOI: 10.1103/PhysRevB.67.024408

PACS number(s): 72.15.Gd, 68.55.-a, 81.15.Fg

I. INTRODUCTION

The discovery of colossal magnetoresistance (CMR) in thin films of ABO₃-type doped manganite perovskites as a consequence of a magnetically driven metal-insulator transition has stimulated numerous investigations of their structure, transport, and magnetic properties, partly because of their interest for device applications in, e.g., sensors or magnetic tunnel junctions.^{1,2} Films may have properties quite different from the bulk materials, due to the extreme sensitivity of the physical properties to structure, oxygen content, and disorder. As a result, the growth method, the deposition parameters, and also the substrate-induced strain will influence the properties. Understanding strain is of particular interest since it can be used to advantage in tuning film properties, as was already demonstrated in cuprates.³ On the other hand, (partial) strain release may induce enough disorder to lead to the occurrence of phase separation, a coexistence of the metallic and the insulating phases.⁴ This is a problem quite specific to the manganites, which derive their properties from the closeness from a first-order phase transition.⁵

In these manganites it has proven difficult to separate strain effects from oxygen doping and disorder, since all three strongly influence the temperature where the metal-insulator transition takes place, as measured by the temperature T_p of the peak in the resistance R . In the case of La_{0.7}Ca_{0.3}MnO₃ (LCMO or L ; pseudocubic lattice parameter $a_p = 3.87$ Å) grown under tensile stress on SrTiO₃ (STO, $a_p = 3.905$ Å), several authors found T_p around 160–180 K [Refs. 6–8], compared to a bulk value around 270 K. It was suggested that this is due to biaxial strain effects.^{9,10} Similar strain-induced decrease of T_p was reported for the case of La_{2/3}Ba_{1/3}MnO₃.¹¹ On the other hand, both the introduction of disorder¹² and oxygen deficiency¹³ yield lowering of T_p of a similar order of magnitude. The question of the meaning of a particular value of T_p in terms of epitaxy or disorder was not yet fully solved.

In this work we address both the issues of strain and strain relaxation. We compare the properties of films of LCMO

grown on (110)-NdGaO₃ (NGO or N , $a_p = 3.87$ Å), which provides a lattice-matched substrate, with films grown on STO ($a_p = 3.905$ Å) and LaAlO₃ (LAO, $a_p = 3.79$ Å), and with films grown on a thin (down to 5 nm) template layer of YBa₂Cu₃O_{7- δ} (YBCO or Y , $a_p = b_p = 3.86$ Å at the growth temperature) first deposited on either nonmatching substrate. The main reason to choose this template is that there are many combinations with potentially interesting properties to be fabricated by combining a high- T_c superconductor with one of the ABO₃-type perovskites. To name two, the superconductor can be combined with a ferroelectric such as (Pb,Zr)TiO₃ in order to have dynamic doping control;¹⁴ or with a ferromagnet such as LCMO in order to study the effects of spin injection.¹⁵ In all cases it is important to know whether strain effects may be at play. We show here that the template is surprisingly effective in relaxing the strain imposed by the substrate. We also compare three-layer samples of STO/ L / Y / L , again with a thin (5 nm) Y layer, with four-layer samples STO/ Y / L / Y / L . The results are strikingly different. The properties of the three-layer sample clearly show the presence of two different L layers, one strained, one unstrained, while the four-layer sample has two fully equivalent L layers. The strain-relaxing layer can therefore be used to avoid inhomogeneity problems connected with partial strain release, but also to engineer different properties of one material in a multilayer.

II. EXPERIMENTS

All films studied were sputter deposited from ceramic targets of nominally La_{0.7}Ca_{0.3}MnO₃ and YBa₂Cu₃O₇ on STO substrate, in a pure oxygen atmosphere of 300 Pa with a substrate-source on-axis geometry. The high pressure leads to a very low growth rate of 1.4 nm/min and 2.5 nm/min for LCMO and YBCO, respectively. Multilayers were grown by rotating the sample from one target position to the other. The growth temperature was chosen at 840 °C, in order to be able to grow high-quality films of both materials at identical condition. Except when noted, the samples were cooled to room

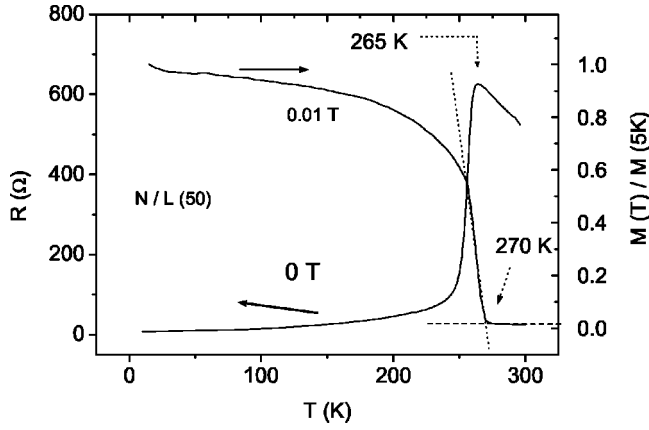


FIG. 1. Resistance R in zero applied field and magnetization M in an applied field of 0.01 T as functions of temperature T for a LCMO film of 50 nm grown on NGO [called $N/L(50)$]. The magnetization is normalized by the value at 5 K, $M(5\text{ K})$. Arrows denote the peak temperature T_p and the Curie temperature T_c .

temperature after deposition without post annealing, which leads to nonsuperconducting $\text{YBCO}_{7-\delta}$ with $\delta \approx 0.53$ (from the lattice parameter). Some were post-annealed for 0.5 h at 600°C in 1 atm of O_2 , resulting in superconducting YBCO_7 ($T_c \approx 90\text{ K}$). Transport measurements were performed with an automated measurement platform; magnetization was measured with a superconducting quantum interference device based magnetometer. The crystal structure and lattice parameters were characterized by x-ray diffraction. The microstructure was studied by high-resolution electron microscopy (HREM).

III. RESULTS AND DISCUSSION

Film growth in this manner and at this temperature yields pseudomorphic and epitaxial films, as was already shown before:^{8,16} at the interface the in-plane axes of the film line up with the axes of the substrate; in case of mismatch, the out-of-plane lattice parameter will adjust to the in-plane strain according to the Poisson ratio of the material. The epitaxial nature is both seen in x-ray diffraction where we find small widths of the rocking curve for the (00 l) reflections (typically less than 0.05°), and in high-resolution electron microscopy (see below). Figure 1 shows the temperature dependence of the resistance and the normalized magnetization of a 50-nm film of LCMO on NGO.

Both measurements show that on this lattice-matched substrate the values of the temperature T_p of the peak in resistance and the Curie temperature T_c are around 270 K, the same value as that of bulk $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$. Additionally, the in-plane and out-of-plane lattice parameters (not shown here) have the same value as in the bulk material, indicating that the film is fully strain free. These results define the basic properties of our sputter-deposited films, and show that no deviation of stoichiometry or oxygen deficiency is present. Furthermore, all films are smooth, without prominent growth defects, as will be shown later.

Figure 2 illustrates the temperature dependence of the resistance $R(T)$ and the normalized magnetization

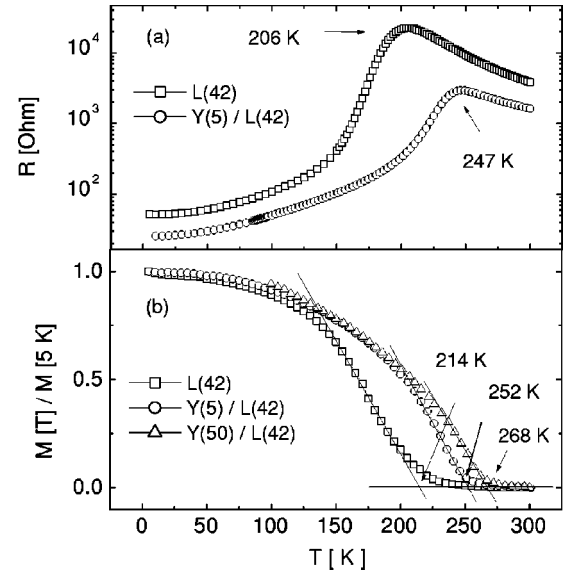


FIG. 2. (a) Resistance R and (b) magnetization M in an applied field of 0.3 T as functions of temperature T for LCMO films of 42 nm grown on STO and on buffer layers of YBCO with thickness of 5 nm or 50 nm (postannealed). The magnetization is normalized by the value at 5 K, $M(5\text{ K})$. Arrows denote the peak temperature T_p and the Curie temperature T_c . In (a), $R(T)$ of $Y(50)/L(42)$ is not given because the Y layer was superconducting.

$M(T)/M(5\text{ K})$ in 0.3 T for a single LCMO film of thickness $d_L = 42\text{ nm}$ on STO, denoted as $L(42)$, and for a LCMO layer of the same thickness on STO with a buffer layer YBCO of thickness $d_Y = 5\text{ nm}$, denoted as $Y(5)/L(42)$. As marked in the figure, T_p can be found from $R(T)$, while the intercept of the linearly increasing $M(T)$ with the constant magnetization at high temperature is used to determine T_c . Clearly, T_p and T_c are almost 40 K higher than for a LCMO film of the same thickness deposited directly on STO. For a postannealed 50-nm YBCO layer [$Y(50)/L(42)$ in Fig. 2] T_c of the LCMO film increases even to 268 K, the value of bulk LCMO.

The lattice mismatch between STO and the smaller bulk LCMO is 0.9%. Growing directly on STO should lead to biaxial tensile strain of the a - c plane of the LCMO epitaxial films, while the value b_p of the out-of-plane pseudocubic b axis should be compressed. Out-of-plane and in-plane lattice parameters were determined from the (002) and (103) reflections, respectively. Figure 3 plots b_p as determined from the strongest reflection of the (002) peak in the diffraction pattern of single films and multilayers as a function of d_L . Films up to 200 nm grown directly on STO show significant compression with b_p around 3.82 Å , much smaller than the bulk LMCO value of 3.87 Å . The strain relaxes only slightly with increasing thickness, indicating that all these films are strained. This strain is quite robust, as seems typical for 1-1-3 perovskites. Postannealing at an elevated temperature (950°C) in flowing oxygen does not yield appreciable relaxation.¹⁷ However, b_p of a 42-nm LCMO layer on a 5-nm YBCO template layer has relaxed to 3.84 Å , while a template layer of 50 nm with post-annealing yields complete relaxation, with both b_p and a_p at the bulk value of 3.87 Å ;

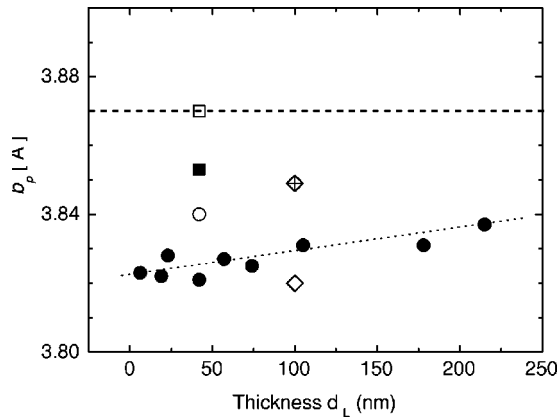


FIG. 3. The out-of-plane lattice parameter b_p of the LCMO layer as a function of LCMO film thickness d_L for single films of LCMO on STO (●), on a 5-nm YBCO layer (○), and on 50-nm YBCO layers without (■) or with (□) postanneal; also for a three-layer sample $L/Y/L$ (◇, two values) and a four-layer sample $Y/L/Y/L$ (+). The dashed line denotes the bulk value of b_p , the dotted line is meant to guide the eye.

for comparison, a 42-nm-thick LCMO film grown directly on STO has a_p at the substrate value of 3.91 Å. The lattice mismatch between YBCO ($a_p = b_p = 3.86$ Å at the growth temperature) and STO is also quite large, but apparently YBCO can effectively accommodate the strain imposed by the substrate within a few nanometers.

More about the differences of growing LCMO on substrate or template can be learnt from electron microscopy. The lattice mismatch between LCMO and YBCO is small, and should lead to little strain in the LCMO layer when grown on unstrained YBCO.

Figure 4 shows HREM pictures of 42-nm LCMO films with [Figs. 4(a, b)] and without [(Fig. 4(c, d))] an YBCO template layer of 5 nm. The LCMO film grown directly on STO is epitaxial and smooth, with a twin structure of b axes pointing in the three major crystallographic directions (not shown). The YBCO template layer [Fig. 4(a), inset] actually is islandlike. Nevertheless, the LCMO film is perfectly ordered, and has regained its smoothness. In the area investigated by HREM only one direction of the b axis was observed. HREM indicates that the strain relaxation really takes place *inside* the YBCO layer, rather than that it is mediated by dislocations in the LCMO layer.

Still, even with the data from electron microscopy, the role of the template is difficult to assess. For instance, the STO terminating layer may play a role: it was recently shown that on specially prepared singly terminated surfaces (either SrO or TiO₂), the initial growth is two-dimensional (2D), but that relaxation and island growth sets in at a thickness of around 6.5 nm (SrO termination), or 20 nm (TiO₂ termination) layer.¹⁸ Also, the starting layer for the YBCO is different for the two substrate termination layers.¹⁹ We do not observe 2D growth, which may have to do with the mixed nature of our STO termination layer. To confirm this, we also measured the c -axis lattice parameter for the 5-nm YBCO layers. On the singly terminated surfaces, the pseudomorphic 2D growth was shown to lead to values larger than

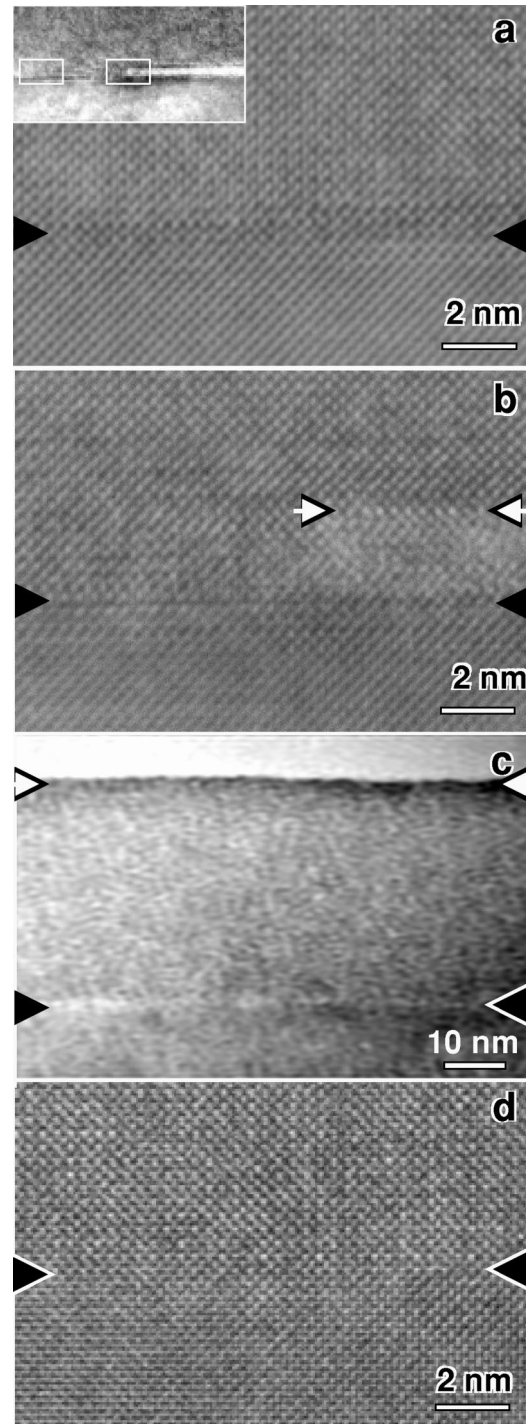


FIG. 4. Electron microscopy images: (a) (b) LCMO film of 42 nm grown on a YBCO layer of 5 nm on top of a STO substrate. The inset in (a) shows the islandlike nature of the YBCO film. (a) is a high-resolution picture from an area without YBCO coverage (left-hand rectangle in inset); the interface is marked with black arrows. (b) shows part of a YBCO island (right-hand rectangle in inset); the interfaces are marked with black and white arrows. (c) (d) LCMO film of 42 nm grown directly on top of a STO substrate; (c) is a low-resolution image in which all high-frequency information (including that of the lattice) is filtered out. The absence of strong contrast at the interface or elsewhere indicates the absence of misfit dislocations (d) is a high-resolution picture of the interface.

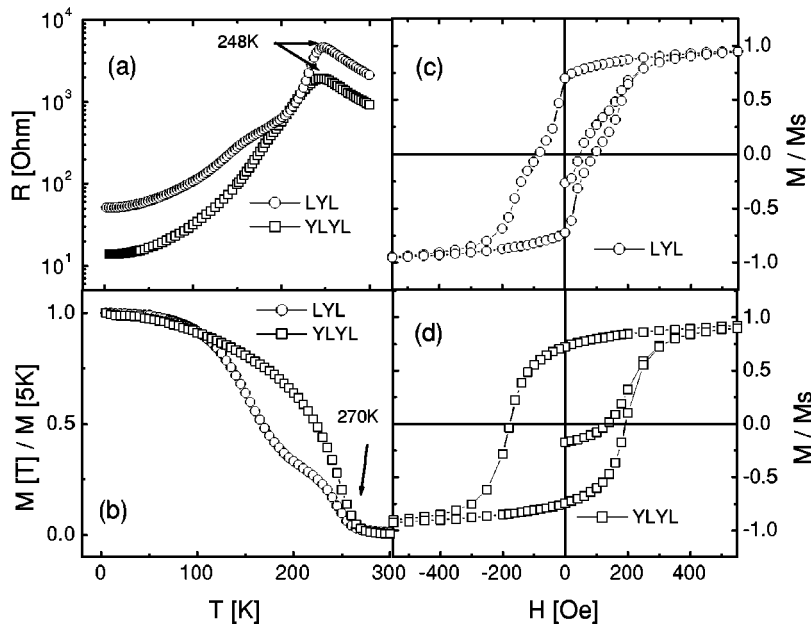


FIG. 5. Behavior of the resistance R and the magnetization M for the three-layer sample $L/Y/L$ and the four-layer sample $Y/L/Y/L$. (a, b) R , M in an applied field of 0.3 T as a function of the temperature T . The magnetization is normalized by the value at 5 K, $M(5\text{ K})$. (c, d) M normalized by the saturation magnetization M_s as a function of applied field H at a temperature of 5 K.

found in the bulk (typically 1.173 nm versus 1.168 nm), which was ascribed to the layer growing in the tetragonal rather than in the orthorhombic phase.¹⁸ We find very broad (005) reflections, with values in the range 1.16–1.17 nm, somewhat below the bulk value. Again, this indicates the template is not 2D and pseudomorphic, but rather consists of islands with a lattice structure close to bulk YBCO. The reason for this probably is that the layering in YBCO, which misses the corner-sharing structure of the oxygen octahedra in the cubic perovskites, makes it easier to regain bulk growth after a disordered initial phase.

The fast strain relaxation by the YBCO template can also be illustrated by the properties of multilayers, for which we investigated three-layer and four-layer samples of a sequence of $\text{STO}/L/Y/L$ and $\text{STO}/Y/L/Y/L$, with values for d_Y of 5 nm and d_L of 100 nm. If the mechanism works as suggested, we can expect that in the former sample the two LCMO layers have different T_p and T_c , because of the different strain states with and without underlying buffer YBCO layer, while in the latter sample the two LCMO layers should have the same properties.

Figure 5 shows the resistance R and magnetization M in 0.3 T as functions of temperature, and the magnetization loops for the three-layer sample and the four-layer sample. From Figs. 5(a, b) it can be seen that the three-layer sample shows two separate transitions both in $R(T)$ and in $M(T)$, as marked with arrows, which correspond to the top and bottom LCMO layer. For the four-layer sample there is only one transition, which indicates that the top and bottom LCMO layers have the same properties. Note that the higher transition temperature of the three-layer sample is the same as the transition temperature of the four-layer sample.

The low-field hysteresis behavior measured at 5 K is also given in Fig. 5. The three-layer sample [Fig. 5(c)] has a small loop with two different coercivity fields; the four-layer sample [Fig. 5(d)] has one coercivity field and a somewhat broader loop. Again, it appears that the three-layer sample contains two layers with different strain states leading to dif-

ferent magnetic loops,⁶ while in the four-layer sample the layers are identical. The reason for the difference in width is not fully clear, but may be due to the difference in microstructure. Finally, information about strain states in both samples also comes from the x-ray data (see Fig. 3). For the three-layer sample we find two separate (002) peaks, with values for b_p of 3.849 Å and 3.817 Å, which should correspond to a more relaxed top layer and a still strained bottom layer, respectively. The full width at half maximum of the peaks is 0.184° (top layer) and 0.057° (bottom layer). In the four-layer sample we find only one set of peaks, yielding a b_p of 3.850 Å, very close to the value for the top layer in the three-layer sample. These results confirm that the underlying YBCO of thickness 5 nm accommodates the strain imposed by the substrate.

Finally, we find very similar results for LCMO grown on LaAlO_3 (LAO), a substrate with a smaller lattice parameter ($a_p = 3.79$ Å). Usually, growth on LAO is strongly columnar and highly disordered for small thickness, due to the island-like growth.^{6,20} Under the same sputtering conditions as used for sputtering on STO and NGO (where films with CMR properties can be produced down to at least 3 nm) it is not possible to grow films on LAO with CMR behavior below about 50 nm.²⁰ However, we find good morphology and bulk-like properties by growing on the template.

Figure 6 shows $R(T)$ and $M(T)/M(5\text{ K})$ in 0.3 T for a LCMO layer of only 15 nm on a buffer layer of YBCO with thickness 10 nm, grown on LAO. The film shows clear CMR behavior with T_p at 214 K. In strong contrast, a film of the same thickness grown directly on LAO does not show a insulator-metal transition (inset of Fig. 6).

IV. CONCLUSIONS

In summary, the properties of sputter-deposited films of $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ deposited on different substrates unequivocally show the effects of strain on the metal-insulator transition, and on the coercive fields in the ferromagnetic state. We

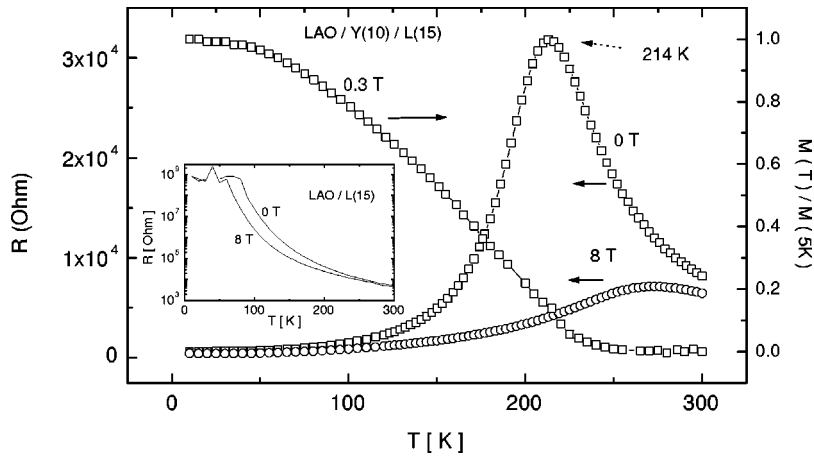


FIG. 6. Resistance R in applied fields 0 T, 8 T, and magnetization M in 0.3 T as functions of temperature T for a LCMO film of 15 nm grown on a buffer layer of YBCO with thickness of 10 nm on a LAO substrate. The magnetization is normalized by the value at 5 K, $M(5\text{ K})$. The inset shows $R(T)$ for a film of 15 nm grown directly on LAO.

also find that the strain imposed by SrTiO₃ is accommodated very effectively by growing on an YBCO buffer layer. Using a buffer layer with a thickness of 50 nm, the strain in a LCMO film of 42 nm is totally relaxed, with the ferromagnetic transition taking place near 270 K. Layered templates such as YBCO, which can deform plastically, may be a quite general tool for strain release of 1-1-3-type materials, especially if no matched substrate is available or in order to avoid complications with different thermal-expansion coefficients of film and substrate. Also, the template can either be used to

grow LCMO layers with identical strain, for instance in magnetic tunnel junctions, or purposely for layers with different strain.

ACKNOWLEDGMENTS

This work was part of the research program of the Stichting voor Fundamenteel Onderzoek der Materie (FOM), which is financially supported by NWO. We would like to thank B. Dam for helpful discussions.

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