Interplay of doping and structural modulation in superconducting $Bi_2Sr_{2-x}La_xCuO_{6+\delta}$ thin films

Z. Z. Li and H. Raffy

Laboratoire de Physique des Solides, CNRS UMR 8502, Bât. 510, Université Paris Sud, 91405 Orsay, France

S. Bals and G. van Tendeloo

EMAT, University of Antwerp, Groenenborgerlaan 171, Antwerp B-2020, Belgium

S. Megtert

LURE, Bât. 209D, Université Paris Sud, 91898 Orsay, France

We have studied the evolution of the structural modulation in epitaxial, *c*-axis-oriented, $Bi_2Sr_{2-x}La_xCuO_{6+\delta}$ thin films when varying the La content *x* and for a given *x* as a function of oxygen content. A series of thin films with $0 \leq x \leq 0.8$ has been prepared *in situ* by *rf*-magnetron sputtering and characterized by $R(T)$ measurements, Rutherford backscattering spectroscopy, transmission electron microscopy, and x-ray diffraction techniques. The oxygen content of each individual film was varied by thermal annealing across the phase diagram. The evolution of the structural modulation has been thoroughly studied by x-ray diffraction in determining the variation of the amplitude of satellite reflections in special two axes $2\theta/\theta$-θ scans (reciprocal space scans). It is shown that the amplitude of the modulation along the *c* axis decreases strongly when *x* increases from 0 to 0.2. It is demonstrated that this variation is essentially governed by La content *x* and that changing the oxygen content by thermal treatments has a much lower influence, even becoming negligible for $x > 0.2$. Such study is important to understand the electronic properties of $Bi_2Sr_{2-x}La_xCuO_{6+\delta}$ thin films.

I. INTRODUCTION

Compared to other hole-doped superconducting cuprates with one CuO_2 plane per unit cell, like $Tl_2Ba_2CuO_6$ (Tl-2201) or $HgBa_2CuO_6$ (Hg-1201), the compound $Bi_2Sr_2CuO_6$ (Bi-2201) exhibits two major differences. The first one is its maximum superconducting critical temperature (20 K),[1–3] which is considerably lower than that of Tl-2201 (80 K)[4] or Hg-1201 (94 K).[5] For this reason this compound is very important in the investigation of the normal-state properties of cuprates and paradoxically to the understanding of the mechanism of high T_c superconductivity. The other difference, probably correlated with the first one, is the fact that this compound exhibits an incommensurate structure modulation in the *b-c* plane of displacive behavior.[6] To understand why the Bi-2201 system is so different from other cuprates, the majority of the published works consider the effect of doping,[7–9] which can be achieved in two ways. The first one is by changing the oxygen content in the system.[3] This is sometimes called *mobile* doping.[10] The second way is by using cationic substitution, such as substituting divalent Sr by trivalent La, which decreases the hole content, or trivalent Bi by divalent Pb, which produces the reverse effect.[2,11] This can be called *non mobile* doping. Doping studies show that Bi-2201 is one of the few systems that can be completely investigated from strongly underdoped to metallic overdoped states.[3,12] The T_c value of pure Bi-2201 can vary from 0 to a maximum value T_{cmax} at most equal to 20 K, and that depends strongly on the Bi/Sr ratio. The value of T_c can be raised by nonmobile doping up to 30–35 K using La/Sr substitution and even up to 45 K with simultaneous La/Sr and Pb/Bi substitution.[13,14] The origin of the structural modulation present in the Bi-2201 system is often thought to be due

to the mismatch between the BiO layers and the perovskite slab and/or the presence of extra oxygen.[15] However the relation between the modulation and the extra oxygen is not clear, even controversial. On the one hand, some authors[16] suggest that there is no essential relationship between the incommensurate modulation and extra oxygen. On the other hand, other authors[17,18] suggest that the extra oxygen is the real driving force behind the modulation. In fact, the samples studied were only substituted with La in the former case and only oxygen doped in the latter. Therefore it seems clear that in order to find a possible relation between the modulation and extra oxygen, it is necessary to systematically study both doping situations.

In this paper, we report our results obtained in a systematic study of both nonmobile La doping (from $x=0$ to $x=0.8$) and mobile doping for each La content in Bi(La)-2201 thin films. The use of thin films allows us to easily modify the oxygen content of the samples and to perform transport measurements. The mobile doping levels of these thin films were varied from overdoped to underdoped. The main goal of this study is to show the relation between extra oxygen and the modulated structure for each given La content in the Bi-2201 thin films. The most important issue in the present study is that we show how much La doping influences the amplitude of the structural modulation in these thin films, whatever the oxygen doping.

II. EXPERIMENTAL

Epitaxial *c*-axis-oriented $Bi_2Sr_{2-x}La_xCuO_{6+y}$ ($x=0-0.8$) thin films, 2000–3000 Å thick, were prepared by single target reactive *rf*-magnetron sputtering on heated (720–750 °C) single crystal $SrTiO_3(100)$ substrates and also

TABLE I. Nominal composition of the Bi(La)-2201 targets with various La content and composition of the films measured by RBS

La	Target (Nominal)	Films (RBS)
x	Bi: Sr: La: Cu	Bi: Sr: La: Cu
0	2.00:1.90:0.00:0.90	2.07:1.93:0.00:1.20
0.05	2.00:1.95:0.05:0.90	2.20:1.93:0.07:1.04
0.1	2.00:1.90:0.10:0.90	2.10:1.90:0.10:1.14
0.2	2.00:1.80:0.20:0.90	2.00:1.82:0.18:1.10
0.3	2.00:1.70:0.30:0.90	1.94:1.72:0.28:1.08
0.4	2.00:1.60:0.40:0.80	1.91:165:0.35:1.21
0.5	2.00:1.50:0.50:0.80	2.00:1.50:0.50:1.01
0.6	2.00:1.40:0.60:0.90	1.79:1.40:0.60:1.40
0.8	2.00:1.20:0.80:0.90	1.82:1.14:0.90:1.22

on MgO(100) substrates for composition analysis. The deposition conditions were similar to those previously described for pure Bi-2201 thin films.[3] To prepare films with different x values, a series of targets with the required x values were used. The composition of the films measured by Rutherford backscattering spectroscopy (RBS) on films deposited on MgO is shown in Table I. The measured values of x are quite close to the nominal composition of the target except for x $=0.8$ (about 15% more in the films). Figure 1 presents a high-resolution TEM [110] image of such a film viewed in cross section. The quality of the film-substrate interface is perfect. There is complete epitaxy, no amorphous layer between film and substrate, and no secondary phases formed at the interface.

After deposition the samples were cooled down to 420 °C under process gas. For each x value, the films were studied in four typical oxygen-doping states, spanning the phase diagram, obtained as follows. The so-called as-prepared state was obtained *in situ*: it is close to optimal doping for samples with $0 \leq x \leq 0.4$, which were kept in vacuum at 420 °C for 1 h, while it is an underdoped state for the samples with $0.5 \leq x \leq 0.8$ although they were continuously cooled down

FIG. 1. [110] HRTEM image of an undoped Bi-2201 thin film. The cations are imaged as bright dots under the present conditions.

under O$_2$-rich process gas. The three other doping states were subsequently obtained by *ex situ* annealing treatments of the same sample in different oxygen atmospheres: (i) The samples were partially deoxygenated by an annealing treatment in vacuum at 300 °C for 1 h giving underdoped states. (ii) Then the samples were oxygenated in a pure oxygen flow at 420 °C. (iii) Finally, the samples were exposed in an oxygen plasma at 420 °C with 100% O$_2$ to obtain a still higher oxygenation level. After each treatment, the samples were characterized by the following methods. The superconducting transition temperatures of the films were measured resistively by a standard dc four-probe method and also confirmed magnetically by ac susceptibility measurement with a SQUID magnetometer. The properties of the crystal structure of the films were thoroughly studied by x-ray diffraction (XRD): conventional θ-2θ scan, rocking curve scan, partial pole figure (ϕ-scan), and special two- axes $2\theta/\theta$-θ scan (reciprocal scan) methods were used.

To study the structural modulation in the Bi-2201 system on a local scale, transmission electron microscopy (TEM) has proved to be very useful.[11,19] TEM is certainly a very powerful method, but as it is a destructive technique it does not allow the examination of the evolution of the modulation in the same sample for different oxygen-doping levels. In the present case (a Bi-2201 film on a STO substrate) the preparation of suitable cross-sectional TEM samples was not straightforward because of the limited adhesion of the film to the substrate. An alternative approach is to use x-ray diffraction techniques. For ceramic samples (powder), the structural modulations were studied from standard θ-2θ diffractograms.[20] However this technique is not suitable for thin films because it appears that the modulation amplitude is much less important there than in ceramic samples, resulting in very low diffracted intensities of the same order of magnitude as the background in between average-structure Bragg peaks that are difficult to measure. The situation is worse when the films are highly textured or even epitaxied. For single-crystal samples, the modulated structures were studied using a precession-camera technique.[7] This method is also difficult to use for thin films because of the presence of thick absorbing SrTiO$_3$ substrate. The diffraction volume ratio between film and substrate is inadequate for this transmission
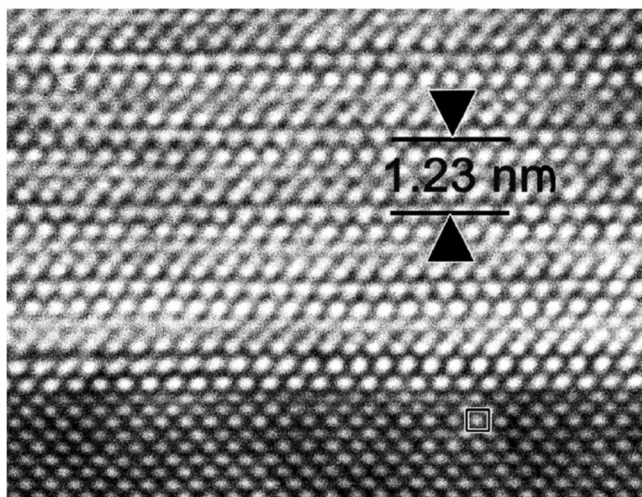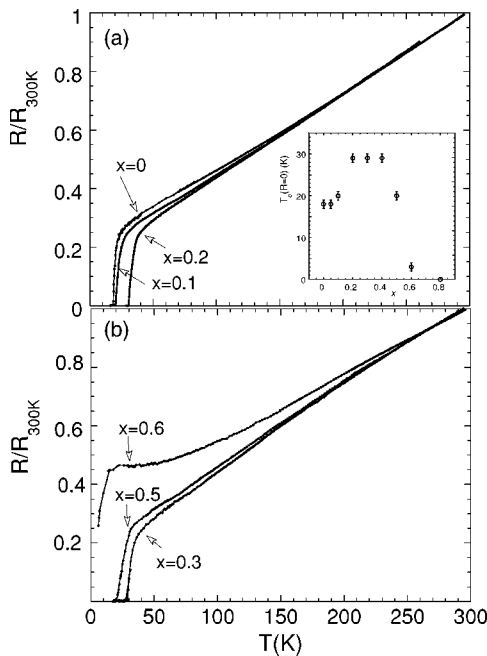
FIG. 2. (a, b) Temperature dependence of the resistance normalized to its value at 300 K, $R/R_{300\,K}$, for $x=0$ to 0.6, of $Bi_2Sr_{2-x}La_xCuO_y$ thin films in the as-prepared state. In insert of Fig. 2(a), $T_c(R=0)$ as a function of x for $Bi_2Sr_{2-x}La_xCuO_y$ thin films in the as-prepared state.

technique. We then used reflection-diffraction geometries on a four-circle diffractometer. Copper radiation was used for this study. A graphite analyzer was mounted in front of the detector (proportional gas counter). As XRD is a nondestructive technique (at least for the kind of samples studied here), we were able to examine the modulated structure of the same sample at different oxygen-doping levels.

III. RESULTS AND DISCUSSION

Figures 2(a) and 2(b) show the temperature dependence of the resistance of $Bi_2Sr_{2-x}La_xCuO_y$ films with $0 \leqslant x \leqslant 0.6$ in the as-prepared conditions. Critical temperature values, $T_c(R=0)$, are about 20 K for $x=0$, 0.05, 0.1, and $T_c(R=0)$ values are up to 30 K for $x=0.2, 0.3, 0.4$.[21] On the other hand $T_c(R=0)$ is equal to 20 K for $x=0.5$ and is less than 4.2 K for $x=0.6$ and for $x=0.8$, the $R(T)$ curve (not shown) exhibits a semi-conducting-like behavior. It is thought that maximum T_c in the La-doped Bi-2201 system occurs for x equal to about 0.4.[22] Therefore the region where x is less than 0.4 is called overdoped. Our results presented in the inset of Fig. 2(a) show that the maximum T_c corresponds to $x=0.2$, 0.3, and 0.4; that is, T_c is maximal over a large compositional range. It is known that in this system T_c is not only dependent on x, but is also dependent on the Bi/Sr ratio. The microstructure plays an important role in the value of T_c as well. In the rest of this paper, we will see that the microstructure distortion because of the incommensurate modulation is attenuated by La doping for $x \geqslant 0.2$. So the large modulation amplitude existing for $x \leqslant 0.1$ could be one of the main reasons to why T_{cmax} is only 20 K in these cases. It should be
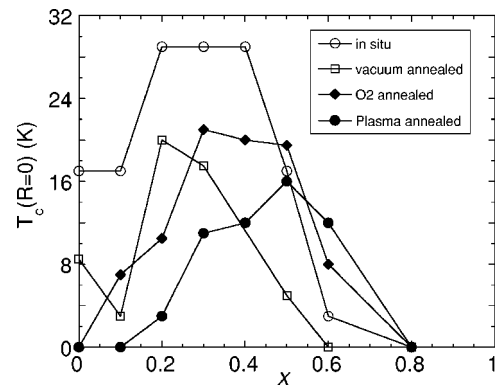

FIG. 3. $T_c(R=0)$ vs x of Bi(La)-2201 films in the different doping states: ○ as prepared, □: annealed at 300 °C in vacuum, ◆: annealed at 420 °C in oxygen flow, and ● exposed at 420 °C in pure oxygen plasma.

noted that a phase transition from monoclinic to orthorhombic occurs for $x \cong 0.1$.[7] Figure 3 allows us to compare the T_c values of the as-prepared (or *in situ*) samples with the values found after the three annealing treatments: deoxygenation in vacuum, oxygenation in O_2 flow, and in oxygen plasma. It appears that for $0 \leqslant x \leqslant 0.4$ the as-prepared samples were optimally doped as T_c decreases under *ex situ* annealing. This is in agreement with the linear variation of $R(T)$ in a large T interval [Fig. 2(a)]. In contrast, for $x=0.5$, $T_c(R=0)$ appears not to be influenced by oxygen overdoping. The reason for this remains unclear. It should be noted that in Fig. 4 of Ref. 22 the T_c value for the same composition is out of the parabola line representing $T_c(p)$, and in Ref. 23, T_c for x equal to 0.5 was only 10 K, whereas it was 33 K for $x=0.4$. For $x=0.6$, the samples were underdoped as $T_c(R=0)$ value increased from $\leqslant 4.2$ K (as-prepared sample) to 8 K and to 12 K when the samples were subsequently treated by annealing in oxygen atmosphere and by exposing in pure oxygen plasma, respectively. For $x=0.8$, after the oxidizing treatments, the film remains semiconducting at low temperature although there is a decrease of the resistance values.

Phase identification, crystal orientation, and film structure were obtained from XRD θ-2θ scans. In all cases the XRD patterns of the films correspond to a single phase as can be seen on a typical XRD pattern given in Fig. 4. The full width at half maximum (FWHM) of the rocking curves through the (008) diffraction peak were always in the range of 0.15 to 0.2°, indicating that all films are highly c-axis oriented (with the c axis perpendicular to the film and substrate surfaces). The epitaxial character is further attested to with the recording of a partial-pole ϕ-scan of the (115) Bragg reflection as shown in Fig. 5. Knowing the parameter c from the earlier θ-2θ scan, the lattice parameter a is deduced from another θ-2θ scan carried out in the reciprocal direction $(h\,0\,3\,\underline{h})$. The variations of lattice parameters c and a of the films as a function of La content are given in Figs. 6(a) and 6(b). It is shown that c decreases and a increases with increasing La content. From Fig. 6(a), we can also see that c decreases with increasing oxygen-doping level for given La content (see also Fig. 2 of Ref. 12). This result is in agreement with those reported for single crystals and for ceramic samples.[7,2] In
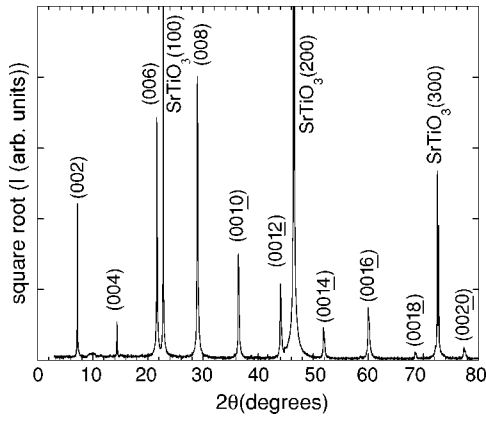
FIG. 4. A typical XRD pattern for a Bi(La)-2201 film. The reflection peaks of $SrTiO_3$ substrate are indicated (the square root of the intensity is plotted to enhance the visibility of low-intensity diffraction peaks).

general, the decrease of the lattice parameter c is thought to derive from the fact that the atomic radius of La is smaller than that of Sr. But from our results or from those of Refs. 7 or 2, the variation of the parameter c between $x=0$ and $x=0.5$, for instance, is much larger than the simple difference of atomic radius between La and Sr. So this explanation is not sufficient. In fact, as we know, in the Bi-2201 system, the lattice parameter c decreases, while increasing the O_2 doping level. The reason for this could be the insertion of extra oxygen in the BiO bilayer. If this is correct, the decrease of lattice parameter c in the La-doped Bi-2201 system is of the same origin: additional oxygen atoms needed for charge equilibrium increase with increasing La content and are also inserted in the BiO layers.

Let us now consider the main results of this x-ray diffraction study. In order to investigate the incommensurate structure modulation in the La-doped Bi-2201 system, scans in reciprocal space were carried out around the (0 0 $\underline{16}$) main Bragg reflection. Typical patterns of this kind of scan are shown in Figs. 7(a)–7(c). These figures show the presence of modulation in all of the Bi(La)-2201 system as signaled by the existence of satellite reflections around a main Bragg peak of the average structure. The position and shape of the
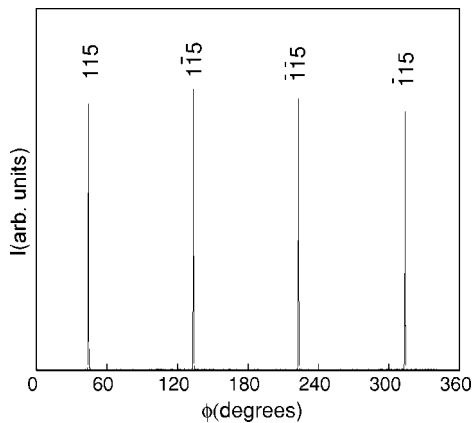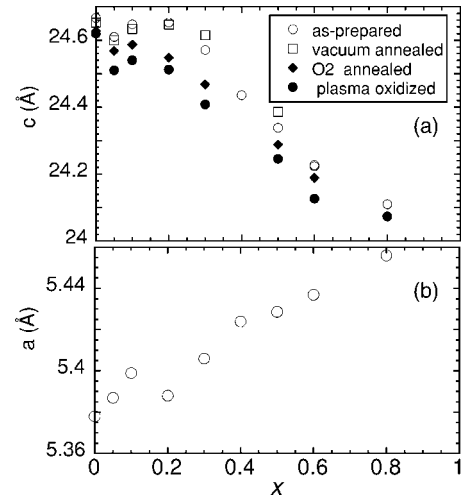

FIG. 6. (a) and (b): Variation of the lattice parameters a and c as a function of x for $Bi_2Sr_{2-x}La_xCuO_y$ thin films in the different doping states (see text).

observed satellites are related to the La content of the as prepared films. In the reciprocal space, the modulation wave vector can be described as $q=(0,q_b,q_c)$. Figure 7(c) shows that for $x \geqslant 0.3$, the shape of the satellite contour becomes elongated. This fact means that there is a loss of long-range
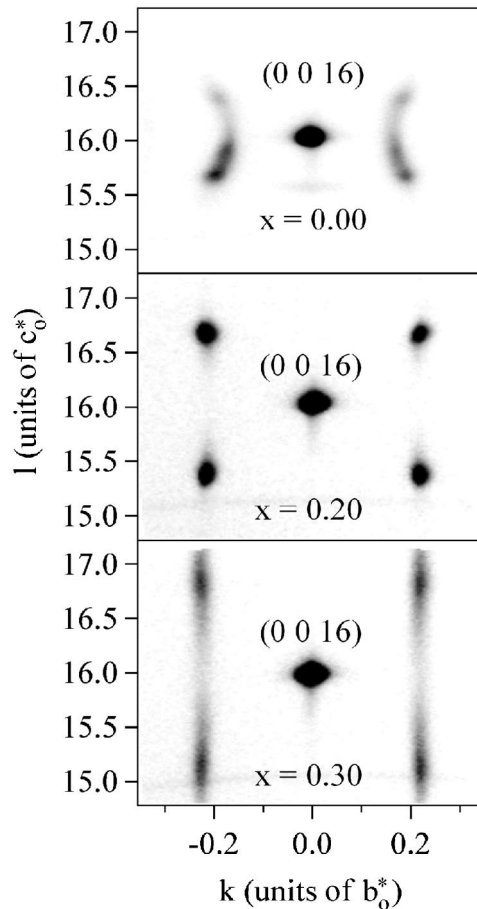

FIG. 7. XRD $\theta/2\theta$-θ scan patterns of Bi(La)-2201 films with (a) $x=0$, (b) $x=0.2$, and (c) $x=0.3$ in the as-prepared state.

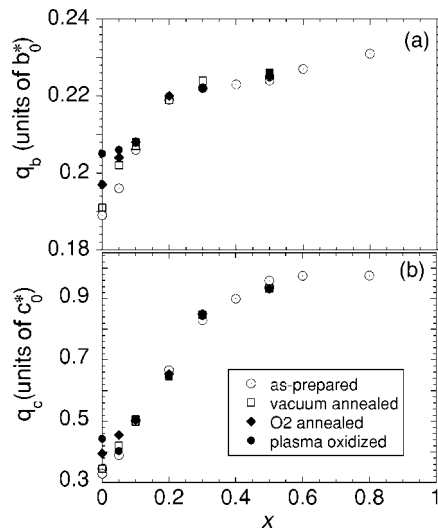FIG. 5. XRD ϕ scan of the (115) reflection of a Bi(La)-2201 film.

FIG. 8. (a, b) q_b and q_c vs x of Bi(La)-2201 films in the different doping states (see text).

order of the atomic displacements along the c axis. Figures 8(a) and 8(b) show the variation of q_b and q_c as a function of La- and O_2-doping levels. In the case of La-undoped Bi-2201 as-prepared samples only, there is a second kind of modulation with $q'=(0,0.17,1)$, which disappears once the samples are annealed (this modulation is no longer present for La-doped even with x as low as $x=0.05$). We can see that q_b and q_c increase monotonically with increasing La content. The results about q_b are very similar to those of Wang et al.[24] For instance, the values of $[q_b(x)-q_b(x=0)]/q_b(x=0)$ were about 13, 18, and 20% for $x=0.2$, 0.3, and 0.6, respectively, in their case, and the values were about 15, 17, and 19%, respectively, in our case. However the superconducting properties are quite different between their ceramic samples and our thin films. We can see also from Fig. 8 that for $x=0$ and 0.05, the values of q_b and q_c increase with increasing O_2 doping level. In contrast, for $x \geq 0.1$, q_b and q_c becomes independent on the O_2 doping level.

Two samples ($x=0$ and $x=0.3$) have been examined by TEM (Fig. 9). Measurement of the q vectors by electron diffraction reveals $q=(0,0.18,0.34)$ for the $x=0$ compound and $q=(0,0.22,0.82)$ for $x=0.3$. With an accuracy of ± 0.03, these values fit very well with the values determined by x-ray diffraction (see Fig. 8).

As is well known in the case of displacive modulated structures, satellite intensities are related to the amplitudes of the atomic displacements of those atoms involved. For small displacements relative to the cell parameters, the contribution of one kind of atom to the amplitude of the diffracted wave is proportional to the scalar product of its displacement vector $\mathbf{R}=(u,v,w)$ with the scattering vector $\mathbf{Q}=(h,k,l)$. The total diffracted amplitude can be complicated to calculate because of the summation over all of those atoms involved in the modulated structure. But what is left is that the corresponding diffracted intensity (the square of the modulus of the diffracted amplitude) will be low if the displacements are very small, higher if the displacements are larger, but always proportional to the square of the scattering vector
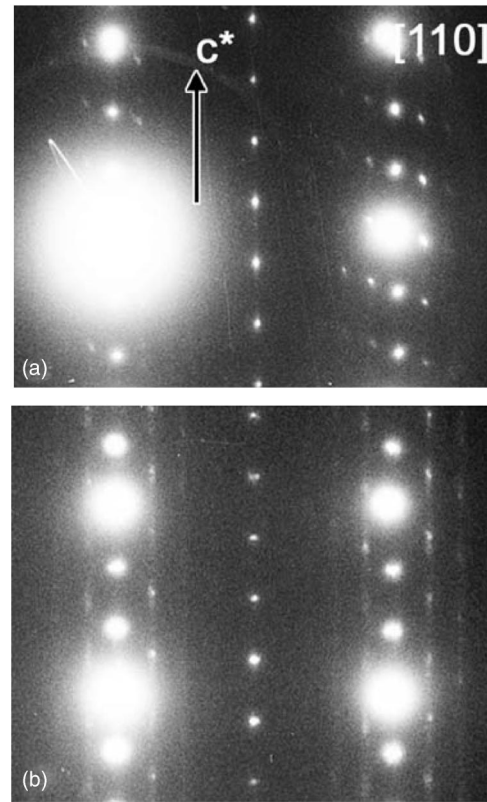

FIG. 9. [110] electron diffraction pattern of (a) the undoped Bi-2201 and (b) the Bi(La)-2201 film with $x=0.3$.

length. Interestingly, as we measured satellite intensities around the Bragg reflection (0 0 $\underline{16}$), we got insight into those atomic displacements that are polarized along c direction, that is, perpendicular to the superconducting CuO_2 planes. Therefore, to measure the behavior of the amplitude of the modulation at large, with respect to the different doping conditions, we took the following quantity as a test probe:

$$(I_s - I_b)/(I_m - I_b),$$

where I_s and I_b are the average values of the integrated intensities of the satellites and the neighboring background, respectively and I_m is the related main Bragg peak intensity. Figure 10 shows the variation of the modulation amplitude as a function of La content and doping level. The results demonstrate that the modulation amplitude decreases with increasing La content up to $x=0.3$. Then above $x=0.4$ the amplitude increases again slightly. It should be noted that the value of the lattice parameter a for the smallest modulation amplitude coincides with that of the Bi-2212 compound, where the amplitude of the modulation is known to be very small in thin films. It is also to be noted that for a given x the modulation amplitude increases with increasing O_2 doping level for $x=0$, 0.05 and 0.1. In contrast for $x \geq 0.2$, the amplitude appears to be independent of the O_2-doping level. Whatever the oxygen content the minimum of the modulation amplitude occurs for $x=0.3$-0.4. So from the comparison of Fig. 10 and 3 giving $T_c(x)$, there appears to be some
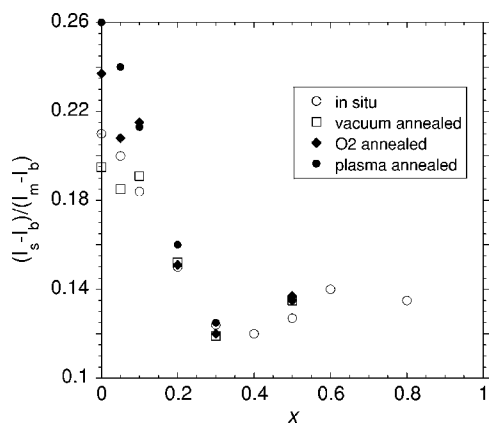
FIG. 10. Reduced satellite intensity $(I_s - I_b)/(I_m - I_b)$ vs x of Bi(La)-2201 film in the different doping states. Subscripts s is for satellite, m for main Bragg reflection peak, and b for the nearby background.

correlation between the occurrence of the maximum of $T_c(x)$ and the minimum of the modulation amplitude.

Several models aiming at the explanation of the origin of the structural modulation are summarized in Ref. 15. Here we focus only the relation between the extra oxygen and the modulation. From Figs. 8 and 10, it can be seen that it is only for $x < 0.1$ and for the higher oxygenation levels that the modulation depends on the extra oxygen. In the La-doped Bi-2201 compounds, the extra oxygens located in the double BiO planes can be divided into two kinds of oxygen. One is used for doping the CuO_2 planes and the second one, the so-called additional oxygen, is used for charge equilibrium as a consequence of the substitution of the divalent Sr by trivalent La atoms. For $x < 0.1$, the extra oxygen is mostly used for doping the CuO_2 planes. The higher oxygen-doping level states with no superconducting transition down to 4.2 K can be easily obtained. However, further increase of the La content leads to an increase of the additional oxygen, which occupies more and more of the BiO planes.[8] This may be the reason why the values of q_b and q_c increase with increasing La content (Fig. 8). The fact that additional oxygen occupies more and more room leads to the fact that the space left in the Bi_2O_2 bilayer for the oxygen used for doping the CuO_2 planes is less and less important. Consequently, oxygen overdoping becomes more and more difficult. As a matter of fact, for $0.1 < x < 0.5$ the most oxygenated states always exhibit a superconducting transition and their T_c values increase with x (Fig. 3), and for $x > 0.6$ the overdoped region even cannot by reached by oxygenation.

In summary, by a systematic study of both nonmobile La doping (from 0 to 0.8) and mobile O_2 doping for each given La content in Bi-2201 thin films, our main results show that: (i) T_c optimum corresponds to $0.2 \leqslant x \leqslant 0.4$ and not only to $x = 0.4$; (ii) for $x < 0.1$ and for the higher oxygen-doping levels the modulation varies with varying oxygen doping level. In this case, we agree with the authors of Refs. 17 and 18, on the fact that the extra oxygen is the real driving force of the modulation. For $x > 0.1$, the modulation becomes independent of the O_2-doping level. Then we agree with Ref. 16 on the fact that there is no essential relation between the incommensurate modulation and doping. (iii) We have shown that the amplitude of the modulation along the c-axis decreases while La content increases from 0 to 0.3. This result is very important to understand the electronic coupling between CuO_2 layers of the Bi(La)-2201 system and the related anisotropy.[25]

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