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Structure and charge transfer driven by the controlled amount of additional oxygen in cation-stoichiometric $Bi_2Sr_2CuO_{6+\delta}$

F. Jean,[1] D. Colson,[2] G. Collin,[1] N. Blanchard,[1,3] Z. Konstantinović,[2] G. Le Bras,[2] A. Forget,[2] and M. Andrieux[4]
[1]*Laboratoire Léon Brillouin, DSM/DRECAM, CEA-Saclay, 91191 Gif-sur-Yvette, France*
[2]*Service de Physique de l'Etat Condensé, DSM/DRECAM, CEA-Saclay, 91191 Gif-sur-Yvette, France*
[3]*Laboratoire de Physique des Solides, Université Paris-Sud, Bât. 510, 91405 Orsay Cedex, France*
[4]*Laboratoire d'Etude des Matériaux Hors-Equilibre, Université Paris-Sud, Bât. 415, 91405 Orsay Cedex, France*

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Polycrystalline Bi-2201 with stoichiometric cationic ratios has been prepared, and an extensive study for the determination and control of the oxygen content was carried out. The extra-oxygen amount per formula unit, δ in $Bi_2Sr_2CuO_{6+\delta}$, ranged from 0.18 down to 0.10 under appropriate annealing conditions. The evolution of the lattice parameters with the oxygen concentration, featuring a switch in the modulation wave-vector components, is presented. In this range of compositions, T_c varies from 3 K (overdoped) to 10 K (underdoped) through a maximum at 16.5 K, showing that, by fine tuning the oxygen excess, most doping levels are accessible in the nominal, substitution-free, Bi-2201.

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I. INTRODUCTION

As High-T_c superconductors remain the subject of much experimental data collection, continuous efforts dedicated to the careful study of the solid-state chemistry of these compounds is quite important. Among the superconducting cuprates, the single-layer Bi-based compound $Bi_2Sr_2CuO_{6+\delta}$ (Bi-2201) is known to be a challenging system to study, due to the difficulties in obtaining single-phase samples and to its highly variable composition. Indeed, mostly nonideal cationic ratios in Bi-2201 have been reported in the literature since that situation appeared to be predominant in the phase diagram.[1–7] However, the oxide's relatively low T_c and high carrier concentration, spontaneously lying close to the suppression of superconductivity, make the study of Bi-2201 normal-state properties of particular interest. The motivation for the present work was to allow a tracking of the compound properties as a function of the doping level without resorting to different cationic compositions, which thus requires a determination and control of the oxygen content. Very few systematic studies have been achieved for this particular purpose,[8] and the results are dependent on a specific aspect of the Bi-2201 phase, that is the extended solid solution giving rise to the general formula $Bi_{2+x}Sr_{2-y}CuO_z$. The contamination of the strontium site by bismuth being influenced by many parameters such as the initial Bi/Sr ratio in the precursor mix, the synthesis temperature, and the atmosphere composition, it remains one of the most erratic features of Bi-2201, with the consequence of data dispersion and an increased difficulty when general trends have to be evidenced. Therefore, attention should be paid to the fact that nearly stoichiometric Bi-2201 was obtained under a moderately-high oxygen pressure,[9] and more recent reports have pointed out the possibility to achieve a stoichiometric 2:2:1 phase under atmospheric pressure by means of lower sintering temperatures (730–750 °C in air, and 800 °C in pure oxygen).[10,11] Since this phase was found to be superconducting,[9,11] it is worth pursuing to explore the Bi-2201 properties dealing with the "reference" cationic composition.

In this paper, we report the determination and control of the oxygen excess in polycrystalline Bi-2201 exhibiting stoichiometric cationic ratios, and we present the evolution of T_c and lattice parameters, including the modulation period, according to the oxygen content as monitored quantitatively. The samples that we characterize hereafter have been used to study in detail the temperature dependence of the thermoelectric power[12] and electronic susceptibility[13] from the strongly overdoped range to the underdoped range.

II. EXPERIMENT

Polycrystalline $Bi_2Sr_2CuO_{6+\delta}$ was prepared by the solid-state reaction in air of Bi_2O_3, $SrCO_3$ and CuO mixed in stoichiometric amounts. The precursors were fired for 10–12 h at 600 °C as a first step. The powder was then successively heated for several days at increasing temperatures between 700 and 730 °C, with intermediate regrinding in an agate mortar. Powder x-ray diffraction (XRD) was performed after each run, and the synthesis was considered as complete on the basis of two criteria: absence of secondary phase peaks and the non-evolution of the XRD pattern (peak shape and position) when the compound was further annealed.

Oxygen nonstoichiometry in $Bi_2Sr_2CuO_{6+\delta}$ was investigated by thermogravimetric analysis (TGA). Samples (1–3 g) were exposed to various temperatures and oxygen partial pressure (Po_2) ranging from 300 to 700 °C and from 10^{-4} to 1 atm, respectively, and the oxygen exchange was measured. Since TGA yields only weight variations, it is of first importance to ensure that the variation is due to oxygen exchange only, and that the measurements are achieved between thermodynamic equilibria. Therefore, all experiments began by an initial heating at high temperature (depending on the Po_2 used, e.g., 700 °C under $Po_2 = 1$ atm) to allow the desorption of H_2O and CO_2 from the sample and holder, and an isothermal step after slow cooling to leave the compound at equilibrium under well defined T-Po_2 conditions. Absolute oxygen content was determined from the mass loss induced by the reduction of the oxide by hydrogen. Setaram (B60, Labsys) and Netzsch (STA449C) devices were used, coupled with gas distribution systems delivering N_2-O_2 mixtures which were checked with an oxygen analyser, or Ar-H_2 (10% H_2) flow for the reduction experiments.

Samples with a controlled oxygen content were prepared by annealing pellets from the same batch under appropriate conditions of temperature and Po_2, and quenching them without changing the atmosphere composition in a liquid nitrogen-cooled setup. XRD patterns were recorded on a Philips diffractometer (PW1710) using Cu$K\alpha$ radiation, between 10° and 130° every 0.02° with a counting time of 18 s per step. Thermopower and magnetization measurements were performed as already described in Refs. 12 and 13.

III. RESULTS AND DISCUSSION

A. Cationic composition

Our observations confirm the spontaneous contamination of the Sr site by bismuth during the synthesis, but also that it can be forced back by long-time heating at moderated temperature (700–730 °C). After the first few runs, the XRD pattern revealed the Bi-2201 phase and some impurity peaks, the most intense being attributed to $SrCO_3$ ($d \approx 3.54$ Å). Considering, therefore, that all Bi_2O_3 has reacted at this step, the primary reaction can be written

$$Bi_2O_3 + 2SrCO_3 + CuO \xrightarrow{O_2 \text{ in air, } CO_2\uparrow} \frac{2}{2+x} Bi_{2+x}Sr_{2-x}CuO_z + \frac{4x}{2+x} SrCO_3 + \frac{x}{2+x} CuO.$$

In the following thermal cycles, the slow disappearance of $SrCO_3$ and the increase of the c parameter of Bi-2201 were observed on the XRD patterns, as the consequence of x decreasing on the right hand in the equation above, i.e., the progressive replacement of bismuth by strontium in Bi-2201. The key parameter here is time rather than temperature: at 740 °C and higher temperatures phase degradation was unambiguously observed.

As the impurity amount eventually became undetectable by powder XRD, the final composition of the oxide was likely to be very close to the nominal one, $Bi_2Sr_2CuO_{6+\delta}$. No significant deviation from the ideal cationic ratios was detected by electron microprobe analysis. Finally, the cell parameters determined for our samples ($a \approx b \approx 5.37$ Å, $c \approx 24.7$ Å, see below) strongly suggest that actually $x \sim 0.0$ in the formula $Bi_{2+x}Sr_{2-x}CuO_{6+\delta}$, according to the variation of these parameters with the Bi/Sr ratio, as evidenced by many independent studies.[1,2,5,6,7,10,11]

B. Oxygen nonstoichiometry

The amount of adsorbed H_2O and CO_2 on the samples was ~3–6 mg per g of Bi-2201, and the desorption takes several days [Fig. 1(a)]. Heating Bi-2201 in the presence of hydrogen induces the reduction of the cuprate into metals and strontium oxide:

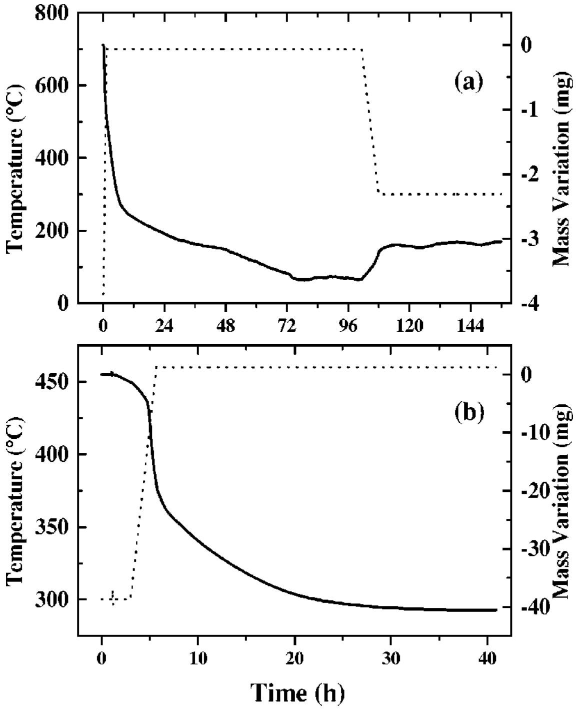

FIG. 1. TGA with a ~0.5-g Bi-2201 sample; mass variation (solid line) and temperature (dot) are represented vs time. (a) Initial heating under $Po_2 = 10^{-1}$ atm. Desorption of adsorbed species (combined with oxygen loss) is observed as the temperature is ramped up to 700 °C, equilibrium being reached after three days. Oxygen uptake occurs as the temperature is lowered. (b) Reduction of Bi-2201 under H_2/Ar flow.

$$Bi_2Sr_2CuO_{6+\delta} + (4+\delta)H_2 \rightarrow 2Bi + 2SrO + Cu + (4+\delta)H_2O.$$

As shown in Fig. 1(b), the temperature was kept low enough to avoid the evaporation of bismuth. It is noticeable that the experiment lasts about four times longer than in the case of Bi-2212.[14] Although the heating rate or the final temperature were not precisely optimized, preliminary experiments showed no significant enhancement of the reaction rate up to 530 °C. The absolute oxygen content of Bi-2201 at 300 °C in pure oxygen was measured seven times and was found to be 6.18 ± 0.04, the error bar being calculated from the statistical distribution. This value is in agreement with that reported by Niinae *et al.*[11] ($\delta \approx 0.20$). Sales *et al.*[15] measured by TGA the oxygen content in $Bi_2Sr_{2-x}La_xCuO_{6+\delta}$, and extrapolating their data to $x = 0.0$ yields $\delta \approx 0.2$. Considering the stoichiometric 2:2:1 phase in the $Bi_{2+x}Sr_{2-y}CuO_{6+\delta}$ system, the same amount is found by Fleming *et al.*[5] according to their titration results. Other estimations[2,6,7,10,16] suggest slightly lower values, in the range 0.14–0.18 extra oxygen per formula unit.

When the samples were exposed to various T-Po_2 conditions, the oxygen exchange appeared as rapid as in other Bi-based cuprates, and equilibria in all cases could be

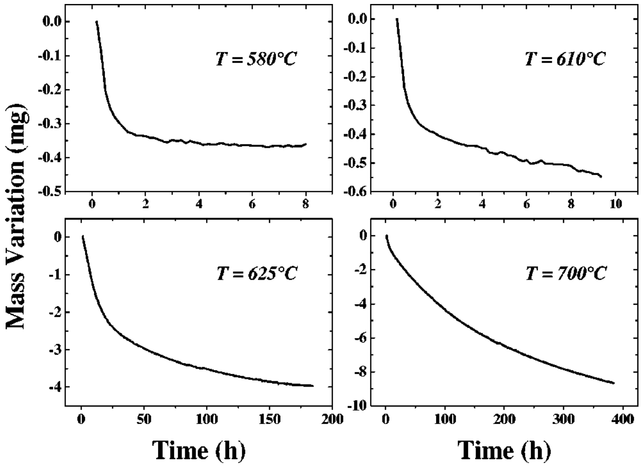

FIG. 2. Thermogravimetric measurements under $Po_2 = 10^{-4}$ atm at various temperatures. Equilibrium is reached at 580 °C and below.

reached in less than 12 h. The reversibility of the changes in composition was checked, and oxygen losses/uptakes were reproducible within 0.002 oxygen per formula unit.

When low Po_2's are used, the decrease of the phase stability limit (740 °C in air) is a strong limiting factor to the extent of the accessible range of compositions. It was not possible to reach equilibrium under $Po_2 = 10^{-4}$ atm at temperatures higher than 580 °C, as can be seen in Fig. 2. Phase decomposition was detected by XRD when long-time treatment was applied. Figure 3 presents the stability region of Bi-2201 according to our TGA and/or XRD results. The decomposition process, which at these temperatures probably consists in the contamination of the strontium site by bismuth, appears significantly slower than the oxygen exchange. Given the large difference in kinetics, some samples were annealed under these severe conditions for further investigation, quenching being achieved after a sufficiently short time (<24 h, typically). In such case, however, no direct determination of oxygen content was made so it was extrapolated from other data established with the quantitatively controlled samples. It had been evidenced in a previous report that the room-temperature thermoelectric power (S_{290K}) varies linearly with oxygen[12] content in the range $0.14 \leqslant \delta \leqslant 0.18$. Measurements of S_{290K} were performed on samples annealed at 700 °C under low Po_2 (10^{-4}-10^{-2}atm), and the oxygen content was determined from the linear fit of the prior data as plotted in Fig. 4. Thus, the diagram in Fig. 5 giving the oxygen excess in Bi-2201 as a function of annealing conditions (T-Po_2) includes both the TGA data and the isotherm at 700 °C, indirectly constructed on the basis of the δ vs S_{290K} relation. The slight difference of reactivity at 300 and 500 °C was confirmed by remeasuring the weight variations under these conditions, and may find its

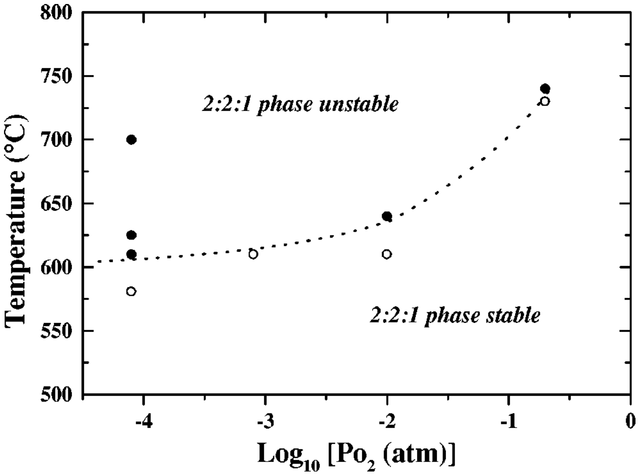

FIG. 3. Bi-2201 stability limit (dotted line) as observed by TGA and XRD. Open circles: phase integrity is preserved. Closed circles: phase alteration was noticed by XRD and/or equilibrium could not be reached during TGA.

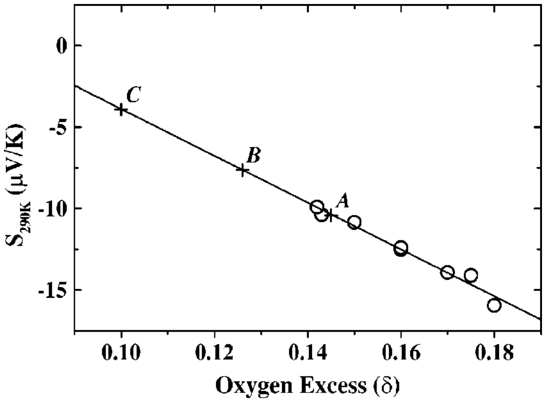

FIG. 4. Oxygen excess vs room-temperature thermopower in Bi-2201. Open circles: S_{290K} has been measured on samples with accurately determined oxygen excess. Crosses: δ in samples annealed at 700 °C under $Po_2 = 10^{-2}$ (A), 10^{-3} (B), and 10^{-4} atm (C) is determined from the linear fit of the prior data after their S_{290K} was measured.

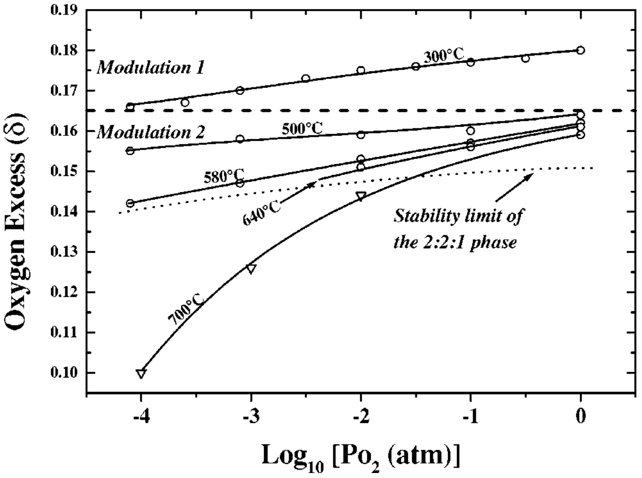

FIG. 5. Oxygen excess δ in $Bi_2Sr_2CuO_{6+\delta}$ as a function of Po_2 and temperature. Open circles show the data collected by TGA, and open triangles mark the compositions determined from the S_{290K} measurements after treatment at 700 °C. Solid lines are only guides for the eye, and the dotted line was drawn according to the data displayed in Fig. 3.

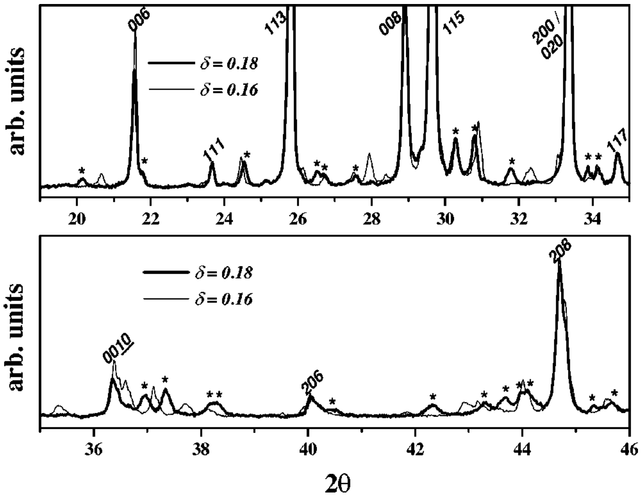

FIG. 6. Parts of the x-ray powder diffraction patterns of Bi-2201 with $\delta=0.18$ and 0.16 showing the two sets of satellite peaks. For clarity, only the satellites for the $\delta=0.18$ phase have been marked by an asterisk.

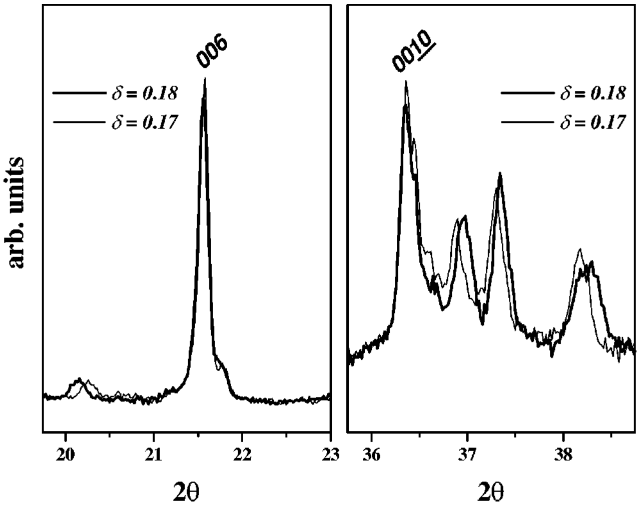

FIG. 7. Parts of the x-ray powder diffraction patterns of Bi-2201 with $\delta=0.18$ and 0.17 showing the dependence of the modulation vector on the oxygen content.

origin in the oxygen-related structural evolution of the system described in the next section. Beside this, the overall behavior of the oxide is consistent with what is generally observed in the Bi-based cuprates, i.e., as temperature increases the isotherms progressively invert their curvature.[8,14,17–19] The values of δ that were determined outside of the stability domain are validated by several concordant observations: satisfactory incorporation of these data in the δ vs (T-Po$_2$) diagram, the induced variation of T_c (see below), the thermopower[12] and the spin susceptibility.[13]

Within the stability domain, the isotherms provide the conditions to cover the overdoped regime in Bi-2201, and the oxygen excess δ can be varied with regular intervals. All the samples having the same cationic composition, this allows one to follow the physical properties as function of a single parameter. Quenching within 24 h has allowed the use of high-T/low-Po$_2$ conditions and thus the study of the Bi-2201 properties at lower doping levels, since further oxygen was actually removed from the host-lattice. One must keep in mind, however, that these phases are metastable and that parameters such as disorder may have an increasing impact.

C. Incommensurate modulation

Powder XRD experiments were systematically performed after thermal treatment, indexation of the peaks being achieved using a monoclinic cell and a modulation vector $\mathbf{q}$ with two incommensurate components along the b and c axes. While the modulation period in Bi-2201 is known to be rather stable along the b axis at $\approx 1/5\mathbf{b}^\star$, the literature provides many different values for the c-axis component in the range 0.3–0.7, depending on the Bi/Sr ratio.[2,5,6,9,10,20–23] Our results indicate that, in addition, a minor change in the amount of inserted oxygen can induce pronounced structural evolution. In fact, two sets of patterns have been clearly distinguished, corresponding to the samples with $\delta=0.18$ and 0.17, on the one hand, and those with $\delta \leqslant 0.16$ on the other hand. Figure 6 shows that, while the average structure remains the same, the satellites due to the modulation have their positions and intensities brutally modified. In the mostly oxygenated phases we found $\mathbf{q}_1 \approx 0.21\mathbf{b}^\star - 0.46\mathbf{c}^\star$ (modulation 1), these components varying with oxygen stoichiometry as illustrated in Fig. 7. In the phases with $\delta \leqslant 0.16$, the modulation vector is $\mathbf{q}_2 \approx 0.19\mathbf{b}^\star - 0.31\mathbf{c}^\star$ (modulation 2), and not further affected by the oxygen concentration unless the annealing conditions stand over the stability limit. Preliminary calculations show that the amplitudes of displacements are similar in the two modes.[24] The lattice parameters determined for the whole series are displayed in Table I. The cell dimensions remain almost unchanged, though smooth variations of the a parameter and monoclinic angle are detectable. The present results are compatible with other reports in which the influence of the post-synthesis annealing on the lattice parameters in cation-stoichiometric Bi-2201 has been examined. Niinae *et al.*[11] observed such a modification of the modulation vector components, from 0.21 to 0.19 along $\mathbf{b}^\star$ and from 0.46 to 0.29 along $\mathbf{c}^\star$ after annealing at 400 °C in argon. Shen *et al.*[25] have shown that at higher temperature (700 °C) the c-axis component further decreases, though we find a greater variation.

The transition between the two differently modulated structures is reversible as additional oxygen is incorporated in the lattice or extracted from it. It is noteworthy that, if a sample is furnace cooled during a typical synthesis process (e.g., in air or flowing oxygen), according to our data the oxygen content will get close to the switch between $\mathbf{q}_1$ and $\mathbf{q}_2$, and either the former modulation or the latter can be observed, depending on the initial temperature, cooling rate, etc. As no indications were given about the cooling processes, this could explain the apparent discrepancy between the results of Khasanova *et al.*[10] and Niinae *et al.*[11] who observed modulations of 2 and 1, respectively, in stoichiometric Bi-2201 prepared in quite similar conditions (flowing oxygen). In addition, chemical heterogeneities (“oxygen-rich” and “oxygen-poor” regions), caused by an out-of-

TABLE I. Oxygen content, annealing conditions, and lattice parameters of Bi-2201 samples quenched after a 24-h treatment. The asterisk indicates an extrapolated value (see the text).

	Annealing conditions	Lattice parameters					
δ	T (°C)/Po$_2$ (atm)	a (Å)	b (Å)	c (Å)	α (°)	q_{b*}	q_{c*}
0.18	300/1	5.365	5.369	24.68	90.03	0.208	-0.473
0.17	425/1	5.367	5.369	24.68	90.04	0.204	-0.438
0.16	$500/10^{-1}$	5.371	5.366	24.65	90.11	0.187	-0.318
0.15	$535/10^{-4}$	5.372	5.366	24.66	90.13	0.187	-0.318
0.14	$580/10^{-4}$	5.375	5.366	24.66	90.15	0.187	-0.317
0.125*	$700/10^{-3}$	5.375	5.364	24.65	90.17	0.177	-0.233
0.10*	$700/10^{-4}$	5.381	5.365	24.67	90.11	0.179	-0.189

equilibrium thermodynamic state, may result in the presence of the peaks of both systems, which was not observed with the quenched samples.

It is generally accepted that the oxygen content depends on the cationic composition, i.e., any modification of the charge balance by chemical substitution is at least partially compensated for by a variation of the inserted oxygen amount. This correlation, however, remaining sometimes unclear, prevents one, for example, from predicting precisely the result of a cationic substitution on the carrier concentration in a given compound. In the present system, deviation from the nominal formula is replacing Sr^{2+} by $3+$ species (bismuth, lanthanum, and rare earth), which will shift the oxygen content towards higher values. From a structural point of view, the composition at which the transition occurs may simply be out of reach by post treatments, as suggested by the unique modulation vector observed in $Bi_{2+x}Sr_{2-x}CuO_z$ as soon as $x \geqslant 0.1$.[11] In return, the occurrence of that transition after soft annealing can be considered as an efficient test to determine if the oxide is actually close to the 2:2:1 composition.

D. Charge transfer

The superconducting transition temperature, as determined from magnetization measurements, is plotted as a function of oxygen excess in Fig. 8. Overdoped, optimal and underdoped ranges are displayed, T_c being maximised at 16.5 K for 0.12–0.13 extra oxygen per formula unit. It is easily seen that if the 2:2:1 phase is synthesized or post-treated using a high pressure of pure oxygen, the compound is likely to be nonsuperconducting ($\delta > 0.18$). On the underdoped side, the use of highly purified inert gas ($Po_2 \leqslant 10^{-5}$ atm) during annealing—rather than a higher temperature—is expected to achieved further decrease of T_c, since according to Fig. 5 a significant oxygen removal would occur.

Since the samples are homogeneous, the 2:2:1 compound is superconducting whether the structure is modulated with $\mathbf{q}_1$ or $\mathbf{q}_2$. Moreover, no steplike evolution of T_c occurs, indicating that the charge transfer is not noticeably affected. The variation of T_c with δ is rapid, consistent with the single-layer situation that is expected to make the additional oxygen particularly efficient as a doping element. In fact, the data can be reasonably fit using the parabolic law of Presland *et al.*[26] $T_c = T_{c_{\max}} \times [1 - 82.6 \times (p - p_{\mathrm{opt}})^2]$, the linear relation $p - p_{\mathrm{opt}} = A \times \delta + B$ being assumed. In the formula $T_{c_{\max}} = 16.5$ K according to our results, and A was fixed to 2 holes transferred to the Cu-O plane by each extra oxygen. The fitting parameter noted B, directly linked to the absolute oxygen content and thus to the experimental difficulty to measure it, was found to be $-0.255(4)$.

As suggested by the evolution of the isotherms ($\partial^2 \Delta / \partial Po_2^2$ changes its sign), it is likely that the defect structure, namely the nature and concentration of punctual defects related to the additional oxygen, is changing in relation with the annealing temperature. The consequence can be a modification of the charge transfer and for a given oxygen concentration one may observe different T_c's, as it was noticed in the Bi-2212 compound,[14] causing again data dispersion between different studies. However, in the case of Bi-2201, because of the lower temperatures used during the post-synthesis treatments, such an effect can be expected to be of lower magnitude.

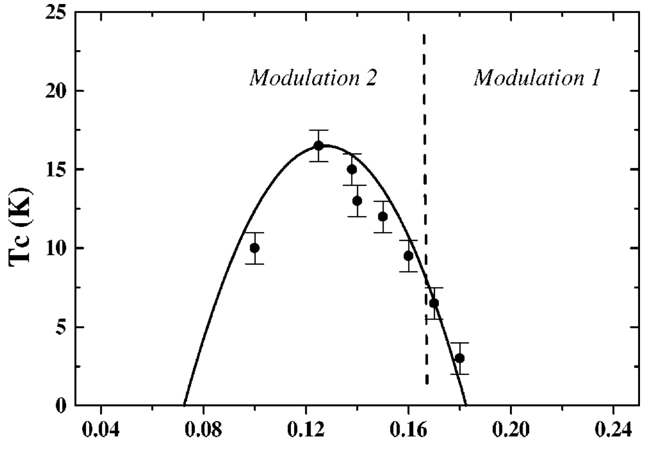

FIG. 8. Evolution of T_c with oxygen excess δ. The solid line was obtained using the parabolic empirical relation (Ref. 25), assuming a linear relation between the hole concentration p and δ, and two holes transferred per additional oxygen (see the text). The dashed line recalls where the change of modulation vector occurs.

Further work has been achieved in the previously mentioned studies of the thermoelectric power[12] and electronic susceptibility.[13] The nonconventional properties of Bi-2201 in the strongly overdoped range are pointed out and analyzed in terms of a growing density of states near the Fermi level as doping increases. In addition, the relation $T_c/T_{c_{\max}}$ vs S_{290K} in Bi-2201 (Ref. 27) has been discussed relative to the other cuprate tendency that was outlined by Obertelli *et al.*[28] A comparison between the experimental data and theoretical previsions is currently in progress.[29]

IV. CONCLUSION

We have determined the conditions to control the oxygen content in polycrystalline cation-stoichiometric Bi-2201. This phase has been stabilized by sintering in air at 700–730 °C instead of the commonly used $T \geqslant 800\,°\mathrm{C}$ temperature range, and its stability limit as a function of oxygen partial pressure has been evidenced. The oxygen excess per formula unit, δ, has been displayed from 0.18 to 0.10, covering most of the superconducting region from a strongly overdoped compound ($T_c = 3$ K) to an underdoped one ($T_c = 10$ K). The monoclinic unit cell appears barely affected by the changes of oxygen content. In contrast, the modulation shows strong correlation to the oxygen concentration, and particularly the c-axis component. Different wave vectors have been identified corresponding to the samples with $\delta \geqslant 0.17$, on the one hand, and samples with $\delta \leqslant 0.16$, on the other hand, the transition between the two modes being reversible. The overall agreement with other studies emphasizes the improvement of reproducibility achieved through a synthesis process and post-treatments that are adapted to the 2:2:1 phase and thus avoid spreading the samples in the complicated Bi-Sr-Cu-O phase diagram.

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