Superconductivity in the La$_2$CuO$_4$–Nd$_2$CuO$_4$ System after Treatment under Oxidizing Conditions

F. Arrouy, A. Wattiaux, E. Marquestaut, C. Cros,[1] G. Demazeau, J. C. Grenier, and M. Pouchard

Laboratoire de Chimie du Solide du CNRS, Université Bordeaux I, 33405 Talence Cedex, France

Two kinds of solid solutions exist in the La$_2$CuO$_4$–Nd$_2$CuO$_4$ system with, respectively, the T/O and T' type structures characteristics of La$_2$CuO$_4$ and Nd$_2$CuO$_4$. When synthesized at atmospheric pressure in air, i.e., under $P \approx 20$ kPa oxygen pressure, both solid solutions exhibit semiconducting properties. A treatment under oxidizing conditions either under oxygen pressure or anodic polarization of La$_{2-x}$Nd$_x$CuO$_4$ compounds causes the insertion of some oxygen species into the T/O structure and the formation of a mixed valence Cu(III)/Cu(II). The resistivity of the corresponding compounds is drastically decreased, and a bulk superconducting behavior is induced at low temperature in the compositional range $0 \leq x \leq 0.60$. For a fixed concentration of excess oxygen, the critical temperature decreases with increasing amount of neodymium. © 1995 Academic Press, Inc.

1. INTRODUCTION

Depending upon the size of the Ln^{3+} ion (Ln, lanthanide element), the Ln_2CuO$_4$ oxides exhibit two different structural types that differ mainly in the respective coordination number (CN) of the two cations. Ln_2CuO$_4$ crystallizes in a distorted K$_2$NiF$_4$-type structure, called T/O, in which the La^{3+} and Cu^{2+} ions are respectively surrounded by nine and six (pseudo-octahedra) oxygen atoms. Most of the other members of the Ln_2CuO$_4$ series (Ln = Nd, Pr, Eu, Gd) adopt a tetragonal-type structure, labeled T', in which the Ln^{3+} and Cu^{2+} ions are respectively in eightfold and fourfold (square planar) coordination (1).

The stability of the A_2BO_4 compounds of the K$_2$NiF$_4$ structure can be predicted from the value of the tolerance factor defined by Goldschmidt in the case of the related perovskite structure

$$t = (r_A + r_O)/\sqrt{2}\,(r_B + r_O),$$

where r_A and r_B are the ionic radii of the two cations and r_O that of the anion O^{2-}. It has been shown from experimental results that the lower limit of t in the case

of the T/O structure is equal to 0.866; for smaller values, the T' structure is observed (2).

Numerous ternary oxides $Ln_{2-x}Ln'_x$CuO$_4$ have also been prepared (2, 3). According to the value of the t factor, which is determined from the average values of the ionic radii of both Ln^{3+} ions, they crystallize either with the T/O or the T' structure. Where the difference in size between the two Ln cations is large (for example with x = 0.80 for Ln = La and Ln' = Dy (2)), a third kind of structure called T*, intermediate between the two previous ones, has been obtained. In this structure, the Cu^{2+} ions are in square pyramidal sites (4).

Previous studies on the La$_2$CuO$_4$–Nd$_2$CuO$_4$ system have shown the existence of two solid solutions with, respectively, the T/O and T' structure. Their domain of stability strongly depends on the conditions of preparation (2, 3, 5). We have previously reported that the insertion of oxygen into the T/O structure of the compound La$_{1.70}$Nd$_{0.30}$CuO$_4$ by means of high oxygen pressure up to 1.6 GPa causes a drastic decrease in the resistivity at low temperature, but it does not induce a bulk superconductivity (6). However, a treatment under 6 GPa oxygen pressure for $x \leq 0.20$ (7), a fluorination treatment for $x \leq 0.30$ (8), or the electrochemical oxidation for $0 \leq x \leq 0.60$ (9, 10) yielded superconducting materials.

In this paper, we report the results of our investigations on the La$_2$CuO$_4$–Nd$_2$CuO$_4$ system prepared in air and on the influence of oxidizing treatments under oxygen pressure and anodic polarization on the structure, the stoichiometry, and the properties of the T/O and T' solid solutions of this system.

2. EXPERIMENTAL

The parent materials La$_2$CuO$_4$ and Nd$_2$CuO$_4$, as well as the intermediate compositions of the system, were prepared by coprecipitation of appropriate amounts of hydroxides–carbonates of the three cations La^{3+}, Nd^{3+}, and Cu^{2+} annealed in air at high temperature. The preparation was described in detail in references (6, 10). The final composition of the samples, determined by microprobe

analysis, proved to be in good agreement with the expected one. Samples in the form of ceramics with 10 to 30% residual porosity were prepared by sintering compacted powders in the temperature range 900–1050°C.

The treatment under oxygen pressure was carried out in an equipment previously described (11). For safety reasons, the maximum oxygen pressure in the autoclave was adjusted as a function of the reaction temperature: $P \approx 120$ MPa at 800°C and $P \approx 40$ MPa at 930–940°C. The samples were enclosed in gold tubes with a small aperture at one end. For some compositions a treatment under much higher pressure was performed in a belt-type press. The oxygen was provided by the *in situ* decomposition of $KClO_3$. The reaction temperature ranged from 1100 to 1300°C and the pressure could be as high as 6 GPa. In order to avoid decomposition of the treated samples, the oxygen pressure has been limited to 1.6 GPa. The resulting potassium chloride was removed from the samples by leaching with water.

The electrochemical treatment was carried out in 1 *M* KOH electrolyte at room temperature in air on sintered pellets of the materials used as working electrodes. A thorough description of the corresponding three-electrodes equipment has been given elsewhere (12). All potentials are referred to the mercury reference electrode (Hg/HgO: $E = 98$ mV/SHE).

The X-ray diffraction (XRD) patterns were recorded with a Philips PW50 spectrometer. The unit-cell parameters were determined on Guinier patterns with silicon as standard. A refinement of the crystallographic data has been performed by the Rietveld profile method from spectra recorded step by step (0.02°) with a counting time of 40 sec. The DBW25 program by Wiles and Young has been used for the calculations (13).

The average oxidation state of copper was determined by iodometric titration. The deviation from oxygen stoichiometry, δ, was calculated by assuming that the excess or deficiency of positive charges was compensated for by the presence of extra O_{2-} anions or oxygen vacancies (14).

The thermal evolution of the resistivity was determined by the four-probe method on sintered pellets (15). The magnetic properties were carried out between 4.2 and 300 K with a vibrating-sample magnetometer having a magnetic field variable from 0 up to 2 T (magnetization vs *H*) and a computerized susceptometer (DSM8 Manics) working under a magnetic field of 1.8 T (susceptibility vs *T*).

3. RESULTS AND DISCUSSION

3.1. Study of the La₂CuO₄-Nd₂CuO₄ System Prepared in Air

The respective stability domains of the T/O and T' solid solutions prepared between 800 and 1000°C at atmo-

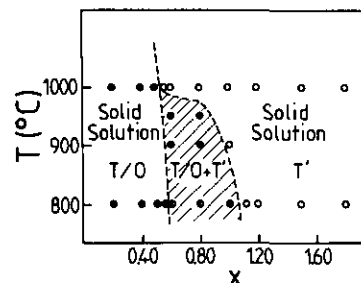FIG. 1. Partial phase diagram of the La₂CuO₄-Nd₂CuO₄ system.

spheric pressure in air ($P_{O_2} = 20$ kPa), according to the procedure previously described, are reported in Fig. 1. The upper limit of x in the T/O type solid solution decreases slightly from 800 to 1000°C. The lowest limit of x in the T' type solid solution is 0.60 at 1000°C instead of 1.00 at 800°C. These results are in good agreement with those previously reported by Manthiram and Goodenough (16) and Bringley *et al.* (17). At high temperature, there is however a discrepency between our data and those of Manthiram and Goodenough: in our case the T' solid solution tends to be stabilized at high temperature, whereas the opposite behavior was observed by the previous authors. This difference comes from the fact that the formation of the T'' phase, isostructural with the T' one, suggested by Manthiram and Goodenough has not been detected in our XRD pattern; therefore, we have made no distinction between the two structures. In any case, the part of the diagram (900 ≤ T ≤ 1050°C and 0.50 ≤ x ≤ 1.00) is rather complicated, because the homogeneity range depends not only on the composition and the temperature, but also on the reaction time and the nature of the precursors. For example, the upper limit of x in the T/O solid solution is only 0.35 when the samples are prepared at 1000°C by solid-state reaction between the oxides Ln_2O_3 and CuO (18).

The variation as a function of the neodymium content x of the unit-cell parameters determined from the XRD patterns for some samples of the T/O and T' solid solutions is reported in Table 1 and Fig. 2. For the sake of comparison between the two different unit-cells, the a parameter of the tetragonal T' cell has been multiplied by $\sqrt{2}$. From these data, the following observations can be made:

(i) in the T/O solid solution, the a parameter decreases with x, whereas b increases; this implies an increase of the orthorhombic distortion as a function of x,

(ii) the a and b parameters in the T/O solid solution are lower than the corresponding one ($a\sqrt{2}$) in the T' solid solution,

(iii) the c parameter in the T/O solid solution is higher than in the T' phase,

TABLE 1

Crystallographic and Analytical Data on Some Compositions of the T/O and T′ Solid Solutions $La_{2-x}Nd_xCuO_{4+\delta}$ Prepared in Air at 1000°C

x (Nd)	Structure type	a (Å) ± 0.005	b (Å) ± 0.005	c (Å) ± 0.005	c/a ± 0.01	V/Z (Å³) ± 0.05	t	δ (± 0.01)
0.00	T/O	5.406	5.370	13.150	2.441[a]	95.43	0.868	0.00
0.10	T/O	5.408	5.356	13.132	2.440[a]	95.09	0.867	0.01
0.20	T/O	5.410	5.350	13.111	2.437[a]	94.88	0.866	0.00
0.30	T/O	5.413	5.345	13.091	2.434[a]	94.69	0.866	0.01
0.40	T/O	5.413	5.342	13.073	2.431[a]	94.50	0.865	0.02
0.50	T/O	5.413	5.339	13.056	2.428[a]	94.32	0.864	0.02
0.60	T′	5.635[b]		12.445	2.208[b]	98.90		−0.03
0.70	T′	5.633[b]		12.420	2.205[b]	98.62		−0.01
0.80	T′	5.631[b]		12.398	2.201[b]	98.29	.	0.00
1.00	T′	5.621[b]		12.350	2.197[b]	97.57		0.00
1.20	T′	5.617[b]		12.320	2.193[b]	97.18		
1.50	T′	5.603[b]		12.265	2.189[b]	96.26		
1.80	T′	5.580[b]		12.200	2.187[b]	94.93		
2.00	T′	5.577[b]		12.171	2.182[b]	94.66		

[a] $a = (a + b)/2$.
[b] $a = \sqrt{2} \times a_{T'}$.

(iv) the c/a ratio and the volume per formula unit is higher in the T/O solid solution.

In order to follow more precisely the influence of increasing amount of neodymium in the T/O structure, a study using the Rietveld profiles method has been carried out on polycrystalline samples of compositions $La_{1.80}Nd_{0.20}CuO_4$ and $La_{1.50}Nd_{0.50}CuO_{4.02}$. By assuming that the space group

FIG. 2. Variation of unit-cell parameters of $La_{2-x}Nd_xCuO_{4+\delta}$ compounds prepared in air at 1000°C (filled circles), after oxygen pressure treatment (open circles), and after electrochemical treatment (T).

is $Bmab$, as in the parent compound La_2CuO_4, a good agreement between the calculated and experimental data has been observed in both cases (Table 2).

The values of the deviation from oxygen stoichiometry δ, calculated from the titration of the average oxidation state of copper, are reported in Table 1. They show that δ is in every case close to zero. However, in the T/O structure, δ is positive for the highest values of x, whereas it tends to be negative for the lowest values in the T′ phase.

In the case of La_2CuO_4, a tolerance factor $t < 1$ creates tensile stresses in the $(La_2O_2)^{2+}$ layers and compressive ones in the $(CuO_2)^{2-}$ sheets (5). These stresses are responsible for a cooperative rotation of the CuO_6 octahedra, which induces an orthorhombic distortion of the structure. Moreover, the oxidation of Cu(II) into smaller (Cu(III) ions inside the $(CuO_2)^{2-}$ sheets resulting from ionic insertion or cationic substitution (Sr^{2+}, Ba^{2+}, ...) in the $(La_2O_2)^{2+}$ layers, relieves the compressive stresses by shortening the average Cu–O bond length. In this way, $La_2CuO_{4+\delta}$ can be made a superconductor with $T_c \approx 40$ K (12, 19–22).

The gradual substitution of neodymium for lanthanum causes an enhancement of the tension in the $(Ln_2O_2)^{2+}$ layers. Consequently, a progressive tilt of the octahedra occurs with increasing x: $\alpha = 4°$ for $x = 0.30$). When x becomes too large, the T/O type structure is no more stable and transforms to the T′ structure. This transformation simply consists of a change in the oxygen-atom positions within the $(La_2O_2)^{2+}$ layers, which leads to a larger Cu–O distance and a change from an octahedral to a square planar environment for the Cu^{2+} ions.
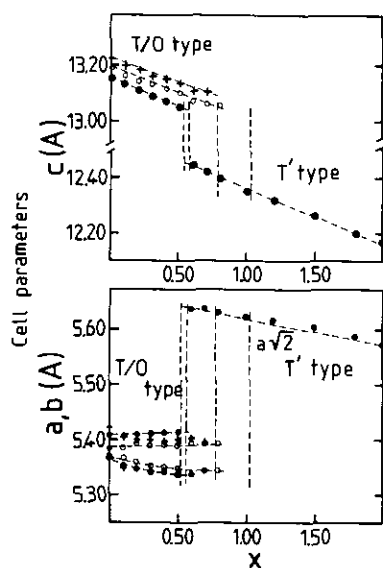
TABLE 2
Crystallographic Data after Refinement by the Rietveld Profiles Method (Space Group *Bmab*)

	Composition	
	La$_{1.80}$Nd$_{0.20}$CuO$_{4.00}$	La$_{1.50}$Nd$_{0.50}$CuO$_{4.02}$
Reliability factors		
R_I (%)	4.50	6.05
R_P (%)	6.04	5.97
R_{WP} (%)	8.27	8.29
Unit-cell parameters		
a (Å)	5.3506(1)	5.3388(1)
b (Å)	5.4102(1)	5.4129(1)
c (Å)	13.1110(2)	13.0564(2)
V/Z (Å^3)	94.884(3)	94.328(3)
(Pseudo-Voigt)	0.6303	0.5970
Atomic positions		
La/Nd	8f	8f
x	0	0
y	0.0086(4)	0.0096(4)
z	0.3613(1)	0.3610(1)
B (Å^2)	0.50(2)	0.38(3)
Cu	4a	4a
$x = y = z$	0	0
B (Å^2)	0.75(6)	0.49(7)
O$_1$	8e	8e
$x = y$	1/4	1/4
z	0.0135(10)	0.0111(19)
B (Å^2)	0.52(17)	1.33(32)
O$_{II}$	8f	8f
x	0	0
y	0.9480(20)	0.9547(28)
z	0.1825(6)	0.1852(7)
B (Å^2)	0.52(17)	0.65(26)

The critical value of x can be predicted from a calculation of the tolerance factor in the Nd$_2$CuO$_4$ structure. If *A*, *B*, and O are spherical ions, the ideal close packing between the CuO$_2$ sheets and the fluorite-type layers is obtained when the ionic radii of the cations obey the relation $(r_A + r_O) = (\sqrt{3}/\sqrt{2}) \cdot (r_B + r_O)$, which leads to the value $t = \sqrt{3}/2 = 0.866$, in very close agreement with the experimental limiting value of the stability of the T/O type structure (2).

As mentioned above, the presence of extra oxygen species would explain why the compounds La$_{1.60}$Nd$_{0.40}$CuO$_{4+\delta}$ and La$_{1.50}$Nd$_{0.50}$CuO$_{4+\delta}$ exist with a T/O structure (Table 1). On the contrary, the T' structure is not stabilized by extra oxygen species because this would increase both the compressive stresses which exist in the $(Ln_2O_2)^{2+}$ layers and the tensile stresses in the CuO$_2$ planes, due to a larger Cu–O distance (5). The T' structure accommodates
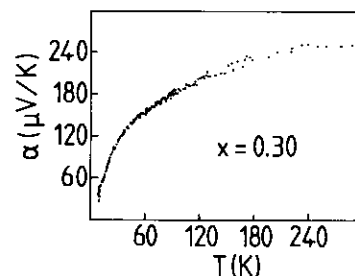

FIG. 3. Thermal variation of the thermoelectric power of La$_{1.70}$Nd$_{0.50}$CuO$_4$.

more easily with an oxygen-deficient lattice, which involves a decrease of the average oxidation state of copper. This could be an explanation for the observed negative values of δ for the composition $x = 0.60$ and 0.80 (Table 1). The tendency of oxygen insertion to stabilize the T/O phase is demonstrated below.

Transport and magnetic properties of the T/O and T' solid solutions. For all the T/O samples, the thermoelectric coefficient α is positive and characteristic of a *p*-type conductivity: for example, α increases from ≈ 10 μV/K at 10 K to ≈ 250 μV/K at 240 K and remains almost constant up to 290 K in the case of the composition $x = 0.30$ (Fig. 3). The thermoelectric power for all the samples of the T' solid solution is negative, which indicates that the charge carriers are electrons, and is higher in absolute value than in the previous case: $\alpha = -850$ μV/K at 298 K for Nd$_2$CuO$_4$. Such a behavior has already been observed by previous authors (23–25) and confirms the results of the chemical titration, i.e., the presence of formal Cu(III) in the T/O compounds and Cu(I) in the T' samples.

The thermal variation of the resistivity of the samples of the T/O type solid solution shows several conductivity regimes (Fig. 4). Below ≈ 170 K, a semiconducting behavior is observed with an activation energy of ≈ 0.01 eV in the temperature range 170–13 K and ≈ 0.001 eV below 13
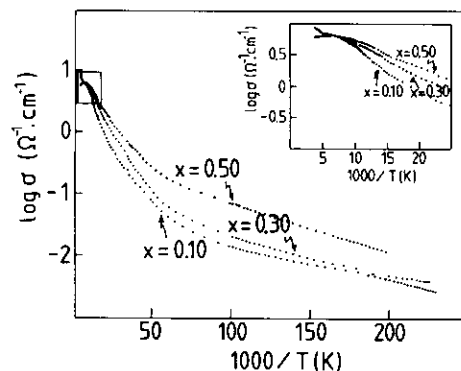

FIG. 4. Thermal variation of the resistivity of some T/O samples.

K. Above 170 K the conductivity decreases with increasing temperature, which implies a metallic type conductivity ($\sigma = 0.138$ Ωcm at 290 K for $La_{1.70}Nd_{0.30}CuO_4$). Such a behavior has been also observed by Singh et al. in the $La_{2-x}Nd_xCuO_4$ and $La_{2-x}Nd_xCuO_4$ and $La_{2-x}Pr_xCuO_4$ solid solutions (3). A semiconducting behavior is observed for all the samples of the T' solid solution, but the resistivity is much higher than in the previous case and decreases with increasing x. The activation energy ($E_a \approx 0.2$ eV) is almost constant for all the compositions.

The thermal evolution of the reciprocal susceptibility of the sample of composition $La_{1.70}Nd_{0.30}CuO_4$ (T/O type) shows that above 120 K the susceptibility follows a Curie–Weiss law with $C = 0.56$ and $\theta_p = -60$ K. At lower temperature there is a gradual deviation from a linear evolution. A similar behavior is observed for all the samples, except that the observed Curie constant increases with the neodymium molar fraction (x). According to previous studies (25, 26), the La^{3+} ions are diamagnetic and the contribution of the Cu^{2+} ions are negligible below 300 K; consequently, the resulting paramagnetic behavior is essentially due to the contribution of the Nd^{3+} ions. From the experimental values of the Curie constant, an effective moment ranging from 3.56 to 3.86 has been calculated, which is close to the theoretical value for Nd^{3+} of 3.68 μ_B.

3.2. Influence of Oxygen Pressure on the Structure and the Properties of the T/O and T' Solid Solutions

Samples with different compositions of the T/O and T' solid solutions, prepared as reported above, have been submitted to treatment under oxygen pressure of 20 MPa $\geq P_{O_2} \geq$ 120 MPa between 800 and 940°C. Following this treatment, a slight modification in the lattice constants of all the samples of the T/O solid solution was observed; it corresponded to an increase in the unit-cell volume and a decrease in the orthorhombic distortion (Fig. 2, open circles). This treatment does not affect the lattice parameters of the T' samples with $x > 1.00$. However, for those with $0.60 \leq x \leq 1.00$, a total or a partial transformation into a T/O structure is observed and is associated with a significant increase in the deviation from oxygen stoichiometry δ (Table 3). In addition, the unit-cell parameters of the so-obtained T/O compounds fit the extrapolated lines coming from the evolution of the a, b, and c parameters in the composition range $x \leq 0.50$, as can be seen in Fig. 2. On the other hand, no change in the stoichiometry of the T' samples ($x > 1.00$) has been observed. In the case of the T/O solid solution ($0.10 \leq x \leq 0.50$), a treatment under oxygen pressure of 120 MPa at 800°C induces an increase in δ up to 0.03 ± 0.01. All these results are consistent with the previously mentioned statement that the T/O structure is stabilized by the presence of extra oxygen species. This effect is clearly illus-

TABLE 3
Extent of Transformation T' → T/O Following the Treatment under 40 MPa Oxygen Pressure for 15 hr at 940°C

x (Nd)	Temperature (°C)	δ ($\pm$ 0.01)	After treatment[a]
0.60	910	+0.03	100% T/O
0.70	920	+0.03	·100% T/O
0.80	940	+0.01	90% T/O + 10% T'
0.90	940		55% T/O + 45% T'
1.00	940		15% T/O + 85% T'
1.10	940		100% T'
1.20	940		100% T'

[a] Estimated from the ratio of the most intense lines of the two structural types in the XRD patterns.

trated by the observed decrease in the orthorhombic distortion (Fig. 2) and by the extension of the stability domain of the T/O solid solution up to $x = 0.70$.

The thermal evolution of the resistivity of the T/O samples shows a quite different behavior before and after the treatment under oxygen, particularly at low temperature (Fig. 5). The resistivity is much lower and decreases suddenly below ≈ 30 K. Such an evolution at low temperature has also been observed in the case of $La_2CuO_{4+\delta}$ ($\delta < 0.03$) (21). The occurrence of a bulk superconductivity in the Nd^{3+} substituted compounds appears to be more and more difficult with rising values of the neodymium content and requires a higher insertion of extra oxygen species. A significant hysteresis has been observed as a function of the cooling rate in the conductivity curves of $La_2CuO_{4.03}$, which has been interpreted in terms of a disproportionation into two phases, one rich and one poor in oxygen (28). The one rich in oxygen induces the presence of enough charge carriers to give rise to a superconducting behavior. In the case of the neodymium-substituted com-
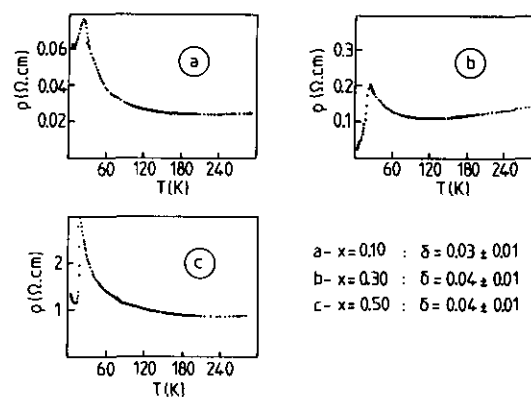

FIG. 5. Thermal variation of the resistivity of some compositions of the $La_{2-x}Nd_xCuO_{4+\delta}$ solid solution after treatment under oxygen pressure ($P_{O_2} = 120$ MPa, $T = 800$°C).
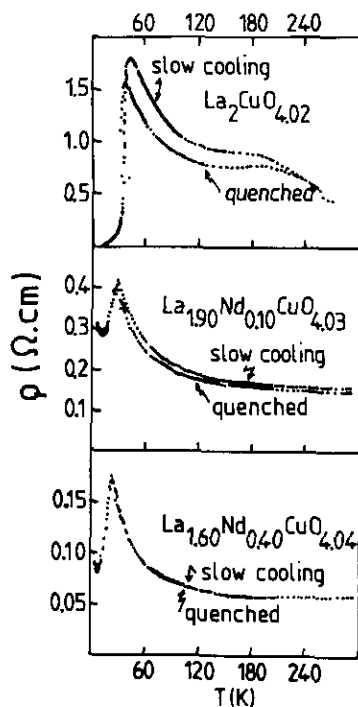
FIG. 6. Thermal evolution of the resistivity of some compositions of the $La_{2-x}Nd_xCuO_{4+\delta}$ solid solution versus cooling rate.

pounds, the hysteresis decreases rapidly and disappears for $x = 0.40$ (Fig. 6), probably because the mobility of the oxygen species below room temperature decreases with the crystallographic c parameter (Fig. 2).

Therefore, in order to increase the δ value, we have carried out some experiments under 1.6 GPa oxygen pressure on the sample of composition $x = 0.30$. A steeper decrease in the resistivity below the onset temperature, as well as a slightly higher value of δ (0.04 ± 0.01), was observed (6), but no diamagnetic signal. We did not use higher oxygen pressure because a partial decomposition was found to occur. However, such experiments have been performed by Takeda et al. under 6 GPa oxygen pressure, which allowed them to reach δ values between 0.08 and 0.09 for $0 \leq x \leq 0.40$. For $0 \leq x \leq 0.20$, a sharp decrease in resistivity has been obtained and a diamagnetic susceptibility observed below ≈ 35 K (7).

3.3. Influence of the Electrochemical Treatment

Next, the electrochemical oxidation developed for the first time in our laboratory for increasing the δ value in the $La_2CuO_{4+\delta}$ compound (12) was applied to some samples of the T/O and T' solid solutions. It proved to have no effect on the unit-cell parameters and the oxygen stoichiometry of the T' samples, but to be effective in the case of T/O compositions.

The voltamperometric curve, performed in standard

pressure and temperature conditions on a ceramic of composition $La_{1.70}Nd_{0.30}CuO_4$ (70% density) is given in Fig. 7. Three different steps are visible: C_I, O_I, and O_{II}. The same electrochemical behavior is observed for all the samples of the T/O solid solution and is in good agreement with that obtained for $La_2CuO_{4+\delta}$ (12). It has been proven that the peak O_I between $500 \leq E \leq 700$ mV (characteristic of a diffusion process) corresponds to the oxidation of the material according to the reaction (12)

$$La_{2-x}Nd_xCuO_4 + \xi\, OH^- \rightarrow$$
$$La_{2-x}Nd_xCuO_{4+\xi/2} + \xi/2\, H_2O + \xi e^-.$$
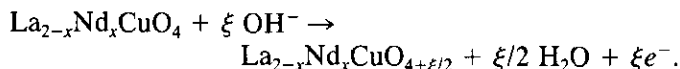
The most favorable conditions, which proved to lead to a bulk oxidation of the samples in 1 M KOH solution, correspond to a potential of 600 mV (Hg/HgO) and a polarization time of at least 15 hr. More details about this oxidation process will be given in a forthcoming paper (10, 27).

An XRD study of the samples after such a treatment shows the following evolution compared to the oxygen-pressure treatment (Fig. 2):

—the a parameter decreases whereas b and c increase,
—the orthorhombic distortion increases, as also does the volume per formula unit.

As in the case of a treatment under oxygen pressure, the oxidation by anodic polarization involves insertion of extra oxygen species into the structure, which is confirmed by chemical titration. As shown in Table 4, an average value of δ close to 0.08 is observed instead of ≈ 0.04 for the previous treatment. However, in contrast to the samples treated under oxygen pressure, the orthorhombic distortion increases after anodic polarization. Such a variation has already been observed for $La_2CuO_{4+\delta}$ and correlated with the amount of additional oxygen. For $\delta \leq 0.05$, the extra oxygen species would be randomly
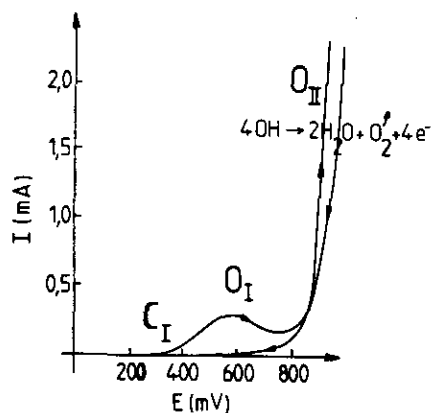

FIG. 7. Voltamperometric curve for a ceramic $La_{1.70}Nd_{0.30}CuO_{4+\delta}$ (70% density).

TABLE 4

Additional Oxygen Content, Critical Temperature, and Diamagnetic Susceptibility for Various Compositions of the T/O Solid Solution, after Electrochemical Treatment (E_{OX} = 600 mV, t = 15 hr)

x	δ (± 0.01)	T_c (K)	$\chi_g \times 10^3$ (emu/g) at $T \approx 4.2$ K
0.10	0.08	39	-1.3
0.20	0.09	35	-3.1
0.30	0.08	32	-3.2
0.40	0.07	29	-2.1
0.50	0.07	26	-1.4

FIG. 9. Thermal variation of the diamagnetic susceptibility of $La_{2-x}Nd_xCuO_{4+\delta}$, measured at 10 mT, after electrochemical treatment (E = 600 mV, t = 15 hr).

located over interstitial sites whereas for $\delta \geq 0.06$, they are ordered (29).

The thermal variation of the resistivity of some samples of the T/O solid solution after oxidation by electrochemistry is given in Fig. 8. All the samples show a metallic behavior and, at lower temperature, a superconducting transition (zero resistivity) that is confirmed by the occurrence of a diamagnetic signal measured under a magnetic field of 10 mT (Fig. 9). A typical thermoelectric power behavior is also given in Fig. 8. In agreement with the chemical analysis ($\delta \approx 0.08 \pm 0.01$), a constant hole concentration is observed over the whole range of composition ($0 \leq x \leq 0.50$).

A similar result has been observed after treatment under 600 mV during 45 hr of a ceramic of composition $La_{1.40}Nd_{0.60}CuO_{4+\delta}$ that has been transformed from a T' to a T/O type structure under oxygen pressure. The corresponding unit-cell parameters have been plotted in Fig. 2. The thermal evolution of the conductivity given in Fig. 10 is consistent with a bulk superconducting behavior at low
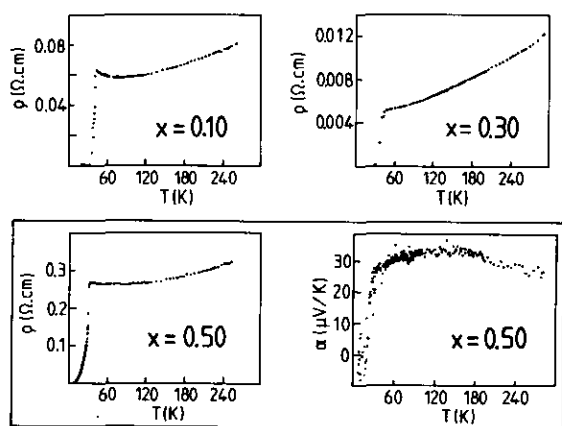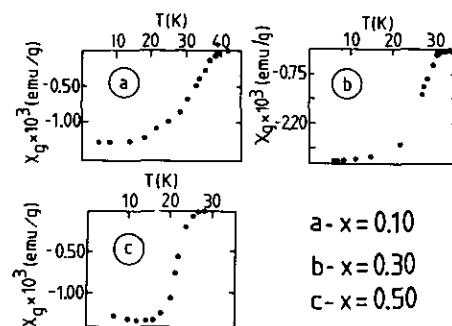
temperature that is confirmed by a negative value of the magnetic susceptibility below T_c: $\chi_g = -0.3 \times 10^{-3}$ emu/g at 4.2 K. The thermal evolution of the conductivity after several electrochemical treatments under 600 mV of the sample of composition x = 0.70 shows only a filamentary type superconductivity in spite of a rather high value of δ (0.08). No diamagnetic signal is observed at low temperature.

In order to study the reversibility of the insertion process of oxygen species through anodic polarization, a sample of composition x = 0.60 with δ = 0.08 was submit-
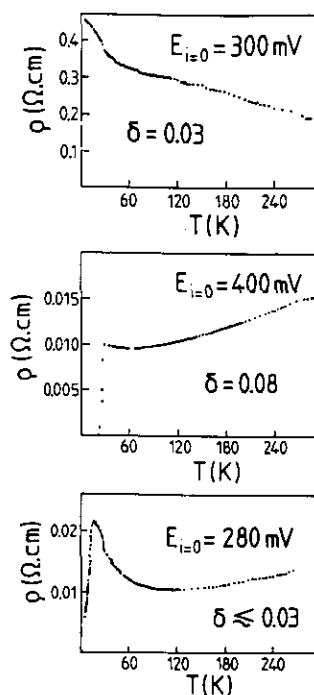

FIG. 8. Thermal variation of the resistivity of T/O type $La_{2-x}Nd_xCuO_{4.08}$ after electrochemical treatment (E = 600 mV, t = 15 hr).

FIG. 10. Thermal variation of the resistivity of $La_{1.60}Nd_{0.40}CuO_{4+\delta}$ after oxygen-pressure treatment (P_{O_2} = 40 MPa, T = 940°C, t = 15 hr), δ = 0.03; after electrochemical treatment (E = 600 mV, t = 15 hr), δ = 0.08; after electrochemical reduction (E = 150 mV, t = 30 hr), $\delta \leq 0.03$.

ted to a cathodic polarization at constant potential lower than the rest potential of the studied compound (equilibrium potential $E_{(i=0)}$) for 15 to 30 hr. A gradual decrease of the value of δ from 0.08 to 0.03 was measured by chemical analysis; at the end, a semiconducting behavior was observed, which confirms the reversibility of the oxygen insertion process (Fig. 10). However, this treatment, which was carried out at room temperature, was not able to induce the transition of the T/O into a T' structure, i.e., the original structure of the sample.

The variation in the critical temperature as a function of the neodymium content x at a constant value of the oxygen excess δ shows a decrease of T_c with x as well as a decrease of the diamagnetic susceptibility (Table 4). A similar variation of T_c has been observed in the $La_{2-x-y}Nd_xSr_yCuO_4$ solid solution (y is constant) (30) and attributed to the decrease in the unit-cell volume, as in the case of the Chevrel phases of composition $LnMo_6Se_8$ (31). This hypothesis can also be considered in the $La_{2-x}Nd_xCuO_{4.08}$ compounds of the T/O type since the unit-cell decreases with increasing x and furthermore the large distance between the Cu^{2+} and Ln^{3+} ions ($d \approx 4.7$ Å) excludes magnetic interactions. Another, perhaps more plausible assumption that could be taken into account is the tendency for oxygen ordering between the La^{3+} and Nd^{3+} ions. Such ordering would imply different crystallographic sites for the two cations: the Nd^{3+} ions would tend to occupy eight-coordinated sites, as in Nd_2CuO_4, which would involve the existence of Cu^{2+} ions with a coordination site lower than 6, due to some missing apical oxygen atoms. Such defects would be responsible for the progressive loss of the superconductive fraction and the decrease in the critical temperature with increasing x.

4. CONCLUSION

The study of the La_2CuO_4-Nd_2CuO_4 system prepared by solid-state reaction in air from the coprecipitated Cu^{2+} and Ln^{3+} hydroxycarbonates has shown that the respective stability ranges of the T/O and T' solid solutions depend not only on the composition and on the reaction temperature (800–1000°C), but also on the nature of the precursors. Furthermore, it should be mentioned that no T* type structure has been observed. A treatment under oxygen pressure up to 40 MPa in an autoclave or 1.6 GPa in a belt-type press of the samples of the T/O structure led to a slight increase in the unit-cell parameters and an increase in the average oxidation state of copper ions, which is consistent with a deviation from the oxygen stoichiometry. The formation of the mixed valence Cu(II)/Cu(III) results in a drastic decrease of the resistivity of the materials at low temperature and in the occurrence of a filamentary superconductivity. Such a treatment does

not affect the T' samples, except those with $0.60 \leq x \leq 0.80$ where a phase transition from the T' to the T/O structure is observed. This structural change is followed by an increase in the δ value from ≈ -0.03 to $\approx +0.03$, which consequently causes a sharp decrease in the resistivity. All these results show that oxygen pressure tends to stabilize the T/O structure through the insertion of extra oxygen species in the $(Ln_2O_2)^{2+}$ sheets; oxygen insertion relieves the tensile and compressive stresses in the structure. However, in our experimental conditions the observed δ value (0.04) is not high enough to induce in the Nd^{3+} substituted compounds a bulk superconductivity at low temperature, in contrast to $La_2CuO_{4.04}$.

The oxidizing treatment by anodic polarization, carried out under standard pressure and temperature conditions, led to δ values close to 0.08 instead of 0.04. Due to these high values of δ, a bulk superconducting behavior could be observed at low temperature for all the samples of the T/O solid solution with $0 \leq x \leq 0.60$. The reversibility of the oxidation process has been demonstrated.

In spite of a high value of δ (≈ 0.08), which apparently leads to a constant hole concentration over the whole range of composition in the Nd^{3+} substituted compounds ($x \leq 0.60$), the critical temperature decreases from 44 K for $x = 0$ to 26 K for $x = 0.60$. This is probably due to the fact that the Nd^{3+} ions tend to occupy crystallographic sites with CN 8, which would imply a CN lower than 6 for some copper ions.

REFERENCES

1. H. Müller-Bushbaum and M. Schweitzer, *Z. Anorg. Allg. Chem.* **428**, 76 (1975).
2. J. F. Bringley, S. S. Trail, and B. A. Scott, *J. Solid State Chem.* **86**, 310 (1990).
3. K. K. Singh, P. Ganguly and C. N. R. Rao, *Mater. Res. Bull.* **17**, 493 (1982); K. K. Singh, Thesis, University of Bangalore, No. 560 012, 1982.
4. S. W. Cheong, Z. Fisk, J. D. Thompson, and R. B. Schwarz, *Physica C* **159**, 407 (1989).
5. J. B. Goodenough and A. Manthiram. *J. Solid State Chem.* **88**, 115 (1990).
6. F. Arrouy, A. Wattiaux, C. Cros, G. Demazeau, J. C. Grenier, M. Pouchard, and J. Etourneau, *Physica C* **175**, 342 (1991).
7. Y. Takeda, K. Yoshikawa, O. Yamamoto, and M. Takano, *J. Solid State Chem.* **92**, 241 (1991).
8. A. Tressaud, B. Chevalier, C. Robin, E. Hickey, and J. Etourneau, *Physica C* **185–189**, 583 (1992).
9. F. Arrouy, A. Wattiaux, C. Cros and G. Demazeau, presented at the "XXIX Annual Scientific Meeting of the European High Pressure Research Group, Tessaloniki, Greece, 21–25 October 1991"; *High Pressure Res.* **10**, 492 (1992).
10. F. Arrouy, Thesis, Université Bordeaux I, No. 779, 1992.
11. G. Demazeau, Thesis, Université Bordeaux I, No. 419, 1973.
12. A. Wattiaux, J. C. Park, J. C. Grenier, and M. Pouchard, *C.R. Acad. Sci. Paris Ser. II* **310**, 1047 (1990).

13. D. B. Wiles and R. A. Young, *J. Appl. Crystallogr.* **14,** 149 (1981).

14. D. C. Harris, and T. A. Hewston, *J. Solid State Chem.* **69,** 182 (1987).

15. P. Dordor, E. Marquestaut, C. Sadulcci, and P. Hagenmuller, *Rev. Phys. Appl.* **20,** 795 (1985).

16. A. Manthiram and J. B. Goodenough, *J. Solid State Chem.* **92,** 231 (1991).

17. J. F. Bringley, S. S. Trail and B. A. Scott, *J. Solid State Chem.* **88,** 590 (1990).

18. A. Manthiram and J. B. Goodenough, *J. Solid State Chem.* **87,** 402 (1990).

19. J. G. Bednorz and K. A. Müller, *Z. Phys. B* **64,** 189 (1986).

20. J. Beille, R. Cabanel, C. Chaillout, B. Chevalier, G. Demazeau, F. Deslandes, J. Etourneau, P. Lejay, C. Michel, J. Provost, B. Raveau, A. Sulpice, J. L. Tholence, and R. Tournier, *C.R. Acad. Sci. Paris Ser. II* **304**(18), 1097 (1987).

21. G. Demazeau, F. Tresse, Th. Plante, B. Chevalier, J. Etourneau, C. Michel, M. Hervieu, B. Raveau, P. Lejay, A. Sulpice, and R. Tournier, *Physica C* **153,** 824 (1988).

22. B. Chevalier, A. Tressaud, B. Lepine, K. Amine, J. M. Dance, L. Lozano, E. Hickey, and J. Etourneau, *Physica C* **167,** 97 (1990).

23. P. Ganguly and C. N. R. Rao, *Mater. Res. Bull.* **8,** 405 (1973).

24. T. Kenjo and S. Yajma, *Bull. Chem. Soc. Jpn.* **46,** 1329 (1973).

25. S. W. Cheong, J. D. Thompson, and Z. Fink, *Physica C* **158,** 109 (1989).

26. M. F. Hundley, J. D. Thompson, S. W. Cheong, Z. Fisk, and S. B. Oseroff, *Physica C,* **158,** 102 (1989).

27. A. Wattiaux, F. Arrouy, C. Cros, G. Demazeau, J. C. Grenier, and M. Pouchard, to appear.

28. J. Ryder, P. A. Midgley, R. Exley, R. J. Beynon, D. L. Yates, L. Afalfiz, and J. A. Wilson, *Physica C,* **173,** 9 (1991).

29. J. C. Grenier, F. Arrouy, J. P. Locquet, C. Monroux, M. Pouchard, A. Villesuzanne, and A. Wattiaux, "Phase Separation in Cuprate Superconductors" (K. A. Müller and E. Sigmund, Eds.), 1994 (in press).

30. J. M. Tarascon, L. H. Greene, W. R. McKinnon, and G. W. Hull, *Solid State Commun.* **63**(6), 499 (1987).

31. M. Sergent, R. Chevrel, C. Rossel, and O. Fisher, *J. Less-Common Metals* **58,** 179 (1978).