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OXYGEN NON-STOICHIOMETRY OF $Nd_{1.85}Ce_{0.15}Cu_{1+\delta}O_y$ AS A FUNCTION OF δ AND ITS RELATION WITH THE SUPERCONDUCTING PROPERTIES

F. Prado, A. Caneiro and A. Serquis

Centro Atómico Bariloche, CNEA, 8400 S. C. de Bariloche, Argentina

Abstract

Thermogravimetric measurements of the equilibrium oxygen partial pressure (P_{O_2}) as a function of the oxygen content y were performed on $Nd_{1.85}Ce_{0.15}Cu_{1+\delta}O_y$ samples with controlled Cu contents ($1+\delta=1.00$, 1.01 and 1.02) at 1173 and 1237 K. The data obtained showed a dependence of the oxygen non-stoichiometry on the nominal Cu content. These measurements are discussed in terms of the presence of Cu defects in the T′ structure. The superconducting response of this material in samples with controlled oxygen and Cu contents was also studied. The superconducting response was found to be very sensitive to the presence of small amounts of cationic and anionic defects.

Keywords: $Nd_{1.85}Ce_{0.15}Cu_{1+\delta}O_y$, oxygen non-stoichiometry

Introduction

The superconductor family $Ln_{2-x}Ce_xCuO_4$ (*Ln*=Nd, Sm, Pr, Eu) was discovered in 1989 by Tokura *et al.* [1]. These compounds have a Nd_2CuO_4-type crystalline structure (T′ phase) in which the Cu cations are square planar coordinated with oxygen anions. Superconductivity is obtained for a small range of doping concentrations x ranging between 0.14 and 0.18. Substitution of Ce^{4+} for Nd^{3+} dopes the CuO_2 sheets with electrons, and earlier Hall and Seebeck measurements confirmed that the charge carriers in the normal state are electrons. However, the presence of a hole band responsible for the superconductivity is suggested and discussed in several papers [2–4].

It is also known that as-made samples are not superconducting and it is necessary to apply additional heat treatment (reduction step) at high temperatures ($1123<T<1423$ K) under a slightly reduced oxygen partial pressure ($10^{-4}<P_{O_2}<10^{-1}$ kPa) in order to obtain superconductivity. It is clear that oxygen is removed during the reduction step. The values reported in the literature for the oxygen loss after this treatment vary between 0.01 and 0.05 per unit formula [5–12]. Some authors have suggested that this oxygen loss corresponds to the creation of oxygen vacancies [5–10], while others indicate that interstitial oxygen atoms are removed during this treatment. There is strong evidence that interstitial oxygen atoms are removed from the apical site of the T′ structure [11–14].

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Accurate oxygen content measurements on as-made and superconducting samples are needed to understand the role of the reduction step and to correlate the physical properties with the oxygen stoichiometry. Different experimental techniques such as thermogravimetry, iodometric titration and neutron diffraction have been used in order to determine the oxygen contents of as-made and reduced samples and the sites of the crystal structure corresponding to the removal oxygen atoms. However, the small amount of oxygen non-stoichiometry accepted by the T′ phase and poorly characterized samples sometimes lead to contradictory results. In particular, the oxygen content determination may be hampered by:

1) the presence of a free CuO excess which is reduced to Cu_2O in the reduction step;

2) inhomogeneous samples and the presence of secondary phases;

3) the possibility of a very small range of cationic non-stoichiometry. It has recently been reported [15–17] that the superconducting response of $Nd_{1.85}Ce_{0.15}Cu_{1+\delta}O_y$ is strongly affected by small variations of the Cu content. Samples prepared by chemical routes with a nominal Cu content slightly higher than 1.00 display a CuO excess and a better superconducting response than those that are stoichiometric or Cu-deficient. This suggests the existence of a very small concentration of defects in the cationic sublattice for a Cu content value close to 1.00. Thus, if such cationic defects do exist, one should expect a dependence of the oxygen non-stoichiometry on the Cu content at around a value of 1.00.

Among the techniques used to determine oxygen non-stoichiometry in oxides, thermogravimetric measurements under a controlled oxygen partial pressure (P_{O_2}) is a powerful tool, since it allows determination of the oxygen content of the T′ phase as a function of temperature and P_{O_2}, and also estimation of the amount of traces of free CuO. From this information, samples with controlled oxygen contents can be prepared by annealing at high temperature under controlled P_{O_2}, with subsequent quenching at liquid nitrogen temperature.

In the present work, we have undertaken a systematic study of the reduction step in $Nd_{1.85}Ce_{0.15}Cu_{1+\delta}O_y$ at 1173 K through thermodynamic measurements of the equilibrium P_{O_2} in samples with nominal Cu contents $1+\delta=1.00$, 1.01 and 1.02 (samples 1.00, 1.01 and 1.02). These results show variations in the P_{O_2} *vs.* y curves for different values of $1+\delta$, suggesting the existence of Cu non-stoichiometry in $Nd_{1.85}Ce_{0.15}Cu_{1+\delta}O_y$, as proposed previously [15–17]. The superconducting responses of $Nd_{1.85}Ce_{0.15}Cu_{1+\delta}O_y$ samples with controlled Cu and oxygen contents were studied through dc magnetization. We confirmed for sample 1.02 that superconductivity is induced suddenly in samples obtained by quenching from 1000 °C under an atmosphere with P_{O_2} just below P_{O_2} for the thermodynamic equilibrium $CuO–Cu_2O$. The Meissner fraction and T_c increase as the oxygen content decreases.

Experimental

Powdered samples of $Nd_{1.85}Ce_{0.15}Cu_{1+\delta}O_y$ with accurately controlled Cu contents were prepared following the metal nitrate decomposition route [15]. The raw materials were 99.999% Nd_2O_3, 99.9% metallic Ce and 99.999% pure Cu. Nd_2O_3

was heated at 1673 K before use for the purpose of eliminating adsorbed or chemically bonded volatile impurities, such as H_2O and CO_2. The raw materials were dissolved in nitric acid at a Nd:Ce:Cu cationic ratio of 1.85:0.15:1. Samples with Cu contents higher than 1.00 were prepared by mixing the previous solution with a titrated solution containing Cu dissolved in dilute nitric acid. Solutions with cationic ratios of 1.85:0.15:1+δ (with $1+\delta=1.00$, 1.01 and 1.02) were prepared in this way. Each solution was stirred and heated until the solvent had evaporated off and annealing treatments in air were then applied at 873, 1073 and 1273 K for 48, 24 and 48 h, respectively.

The final synthesis temperature chosen was 1273 K, just below the eutectic line between $Nd_{1.85}Ce_{0.15}CuO_4$ and CuO [18, 19] (1313 K in air), in order to avoid the formation of a Cu-rich liquid phase in samples with nominal Cu contents higher than 1.00. This partial melting is not recommended since it may affect the cationic composition of the T′ phase [20]. On the other hand, samples with a Cu excess prepared below the eutectic temperature contain pure CuO as secondary phase, which can be detected and estimated by thermogravimetry through the following reaction:

$$2CuO \rightarrow Cu_2O + 1/2O_2$$

which takes place at 900 and 1000°C when P_{O_2} decreases below 1.418 and 1.2×10^1 kPa, respectively [21].

Powder X-ray diffraction (XRD) data were collected on a Philips PW 1700 diffractometer, using CuK_α radiation and a graphite monochromator. The lattice parameters of the T′ phase were calculated from XRD data indexed according to the I4/mmm space group. The values obtained are listed in Table 1.

Table 1 Lattice parameters for samples with different nominal copper contents 1+δ

$1+\delta$	$a=b$/nm	c/nm
1.00	0.3942	1.2075
1.01	0.3946	1.2077
1.02	0.3946	1.2078

DTA curves were recorded with a Netzsch STA 409 analyzer during heating of the samples from room temperature up to 1473 K at a heating rate of 10 K min^{-1} under 1.01×10^2 kPa of pure O_2.

Equilibrium P_{O_2} measurements were performed with thermogravimetric equipment consisting of a symmetrical thermobalance based on a Cahn 1000 electrobalance coupled to an electrochemical system for the measurement and control of P_{O_2}, specially designed for this kind of study [22]. The electrochemical system (zirconia pump and oxygen sensor) [23] provides a controlled Ar–O_2 atmosphere for the thermobalance, with P_{O_2} ranging from 1.01×10^2 to 10^{-4} kPa. The error in P_{O_2} in the Ar–O_2 mixtures can be estimated as ±2%, including systematic error.

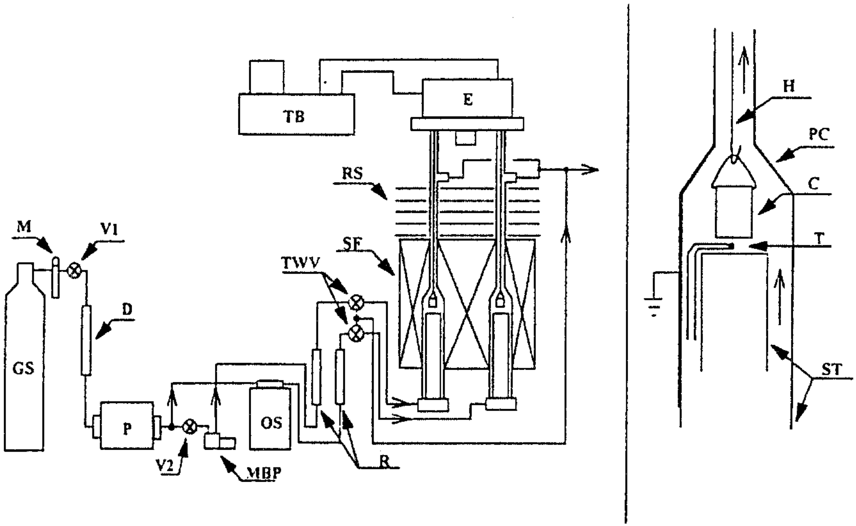
The thermobalance allowed the detection of changes in y within 3×10^{-4} for samples of about 0.7 g of $Nd_{1.85}Ce_{0.15}Cu_{1+\delta}O_y$. The equilibrium criterion verified over the 24 h periods used in this work was constant sample mass with time within 5 μg.

Figure 1a depicts a block diagram of the thermobalance and the electrochemical system. The sample was placed in an Al_2O_3 crucible and suspended from the thermobalance. The temperature was measured by means of an S-thermocouple (Fig. 1b). Each sample was heated up to 1173 K in pure O_2 and the equilibrium mass was determined. P_{O_2} was then lowered at fixed temperature and a new equilibrium value was obtained. This routine was carried out down to $\log(P_{O_2}/\mathrm{kPa}) \sim -3$. For sample 1.02, isotherms were measured at 1173 and 1273 K.

The absolute oxygen content for $Nd_{1.85}Ce_{0.15}Cu_{1+\delta}O_y$ samples was determined thermogravimetrically by reduction in dry H_2 at 1373 K after all the measurements were finished, assuming Nd_2O_3, Ce_2O_3 and Cu as reduction products. The X-ray diffraction data on the reduction products indicated only the presence of Nd_2O_3 and Cu, without peaks of Ce compounds. However, the thermodynamic information on the Ce–O system at 1373 K [24] indicated that the oxidation state of Ce is practically 3.00 under pure H_2 at high temperature. From the accuracy of the Cahn 1000 electrobalance, the error in the absolute oxygen content y was estimated at 0.0025.

The samples with controlled oxygen content were prepared by annealing at 1273 K, under He–O_2 atmospheres with controlled P_{O_2} during 24 h, with subsequent quenching at liquid nitrogen temperature. We assume that there was no change in the oxygen content during the quenching procedure.

The presence of superconductivity was detected through dc magnetization measurements with a Quantum Design DC SQUID magnetometer, the samples being cooled from 25 to 5 K in a nominal magnetic field of 1 mT (ZFC and FC process).



a) b)

Fig. 1 a) Block diagram of the experimental setup. G. S., gas source; M, manometer; V1, V2, needle valves; D, drying column; P, electrochemical pump; G, oxygen sensor; MBP, metal bellow pump; TWV, three-way valve; SF, symmetrical furnace; RS, radiation shields; TB, thermostatic bath; E, electrobalance. b) ST, silica tubes; T, Pt–Pt10% Rh thermocouple; C, alumina crucible; H, hangdown wire; PC platinum coating

Results and discussion

The existence of traces of free CuO in our samples prepared at 1273 K was detected by DTA through the presence of an endothermic peak corresponding to the reaction between CuO and $Nd_{1.85}Ce_{0.15}CuO_y$, which gives rise to a Cu-rich liquid phase at the eutectic temperature. Figure 2 shows the DTA curves for samples 1.00, 1.01 and 1.02 under 1.01×10^2 kPa of pure O_2. Sample 1.00 exhibits neither endothermic nor exothermic reactions from 1273 up to 1423 K. Therefore, this sample is free of CuO within the detection limit of this technique. A very weak endothermic peak is observed at 1352 K for sample 1.01, and a cleaner peak for sample 1.02. These results indicate that samples 1.01 and 1.02 contain traces of excess CuO coexisting with the T′ phase.

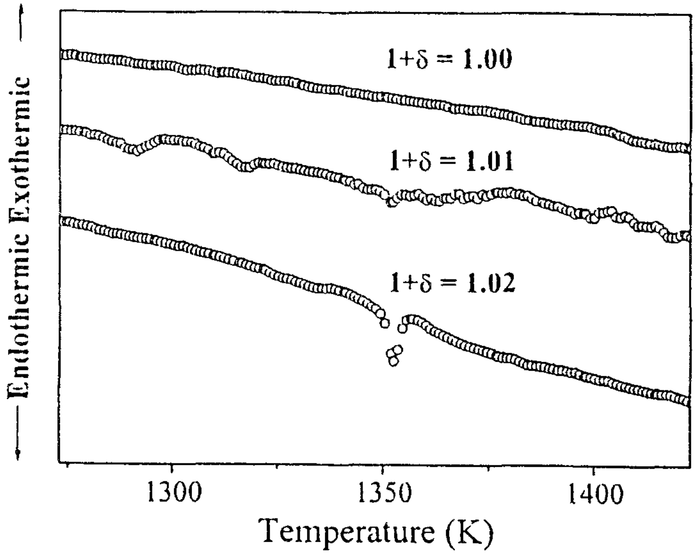


Fig. 2 DTA curves as a function of temperature for samples of $Nd_{1.85}Ce_{0.15}Cu_{1+\delta}O_y$ with $1+\delta=1.00$, 1.01 and 1.02

Figures 3a, b and c present plots of the equilibrium P_{O_2} values as a function of the overall oxygen content y at 1173 K for samples 1.00, 1.01 and 1.02, respectively. In all cases, the curves were obtained by progressive lowering of P_{O_2}. It can be observed that sample 1.00 is free of CuO, while the plots of $\log P_{O_2}$ *vs.* y for samples 1.01 and 1.02 show a small plateau at $\log(P_{O_2}/\mathrm{kPa})\approx0.155$, corresponding to the reduction of traces of CuO into Cu_2O [21]. From the widths of these plateaus, the estimated amount of free CuO is 0.13 and 0.19 wt% for samples 1.01 and 1.02, respectively.

Figure 4 plots $\log P_{O_2}$ *vs.* y for samples 1.00, 1.01 and 1.02. The 1.01 and 1.02 data were corrected for the CuO–Cu_2O phase transition. These curves clearly reveal a dependence of the oxygen content on the nominal Cu content of the samples. The features of the curves for samples 1.01 and 1.02 are similar, but substantially different from those for sample 1.00. Points A, A′ and A″ correspond to the equilibrium P_{O_2} values under pure oxygen for samples 1.00, 1.01 and 1.02, respectively. The oxygen contents at these points increase as the nominal Cu content in-

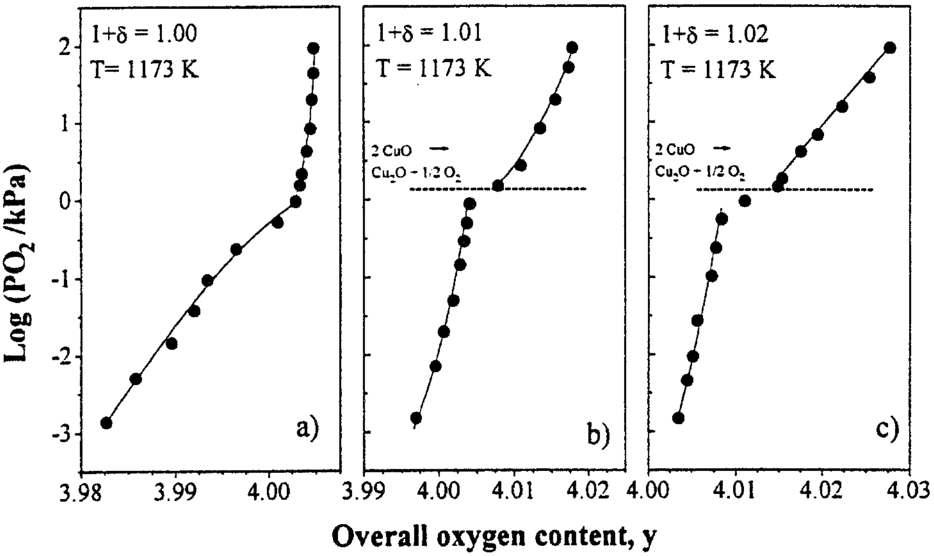


Fig. 3 logP_{O_2} as a function of the overall oxygen content y at 1173 K for $Nd_{1.85}Ce_{0.15}Cu_{1+\delta}O_y$; a) $1+\delta=1.00$, b) $1+\delta=1.01$ and c) $1+\delta=1.02$

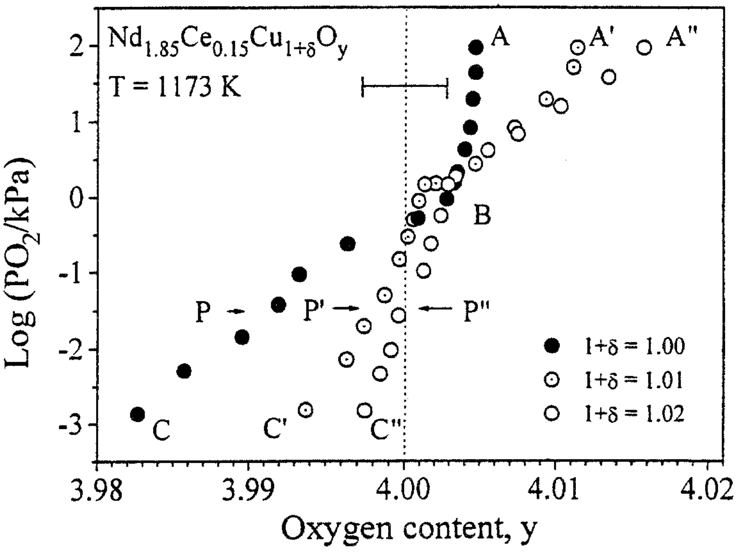


Fig. 4 logP_{O_2} as a function of y at 1173 K for $Nd_{1.85}Ce_{0.15}Cu_{1+\delta}O_y$ with $1+\delta$ values of 1.00, 1.01 and 1.02. The curves for samples 1.01 and 1.02 have been corrected for the CuO–Cu_2O transition. Samples prepared with controlled oxygen content are indicated by points P, P′ and P″

creases. In all cases, the absolute oxygen contents at $P_{O_2}=1.01\times10^2$ kPa are higher than 4.00.

Between points A and B, sample 1.00 exhibits a smaller range of oxygen non-stoichiometry as compared with samples 1.01 and 1.02 (A′–B and A″–B). The periods of time required to reach equilibrium after a change in P_{O_2} between points A and B were appreciably shorter than those for samples 1.01 and 1.02 (parts A′–B and A″–B). The kinetics of evolution towards equilibrium from these two samples is very slow, as discussed previously [13]. The three curves intersect at point B. For samples 1.01 and 1.02, this point corresponds to the thermodynamic equilibrium $CuO-Cu_2O$, while for sample 1.00 the loss of oxygen increases appreciably (part B–C) from this P_{O_2}. The oxygen non-stoichiometry for sample 1.00 in the range $-3.00 \leq \log(P_{O_2}/\text{kPa}) \leq 0.155$ is appreciably larger than those for samples 1.01 and 1.02.

The superconducting response of samples 1.00, 1.01 and 1.02 were studied after they had been annealed at 1173 K under $P_{O_2}=3.04\times10^{-2}$ kPa (points P, P′ and P″ in Fig. 4) over 24 h and subsequent fast cooling to liquid nitrogen temperature. Figure 5 shows the SQUID signal as a function of temperature in a field of 1 mT. No evidence of a diamagnetic signal was detected for sample 1.00, while samples 1.01 and 1.02 exhibited an appreciable diamagnetic signal, which increased as the Cu content was increased. The lack of superconductivity of sample 1.00 can not be related to poor deoxygenation since this sample displayed the lowest oxygen content.

The variations in either the $\log P_{O_2}$ *vs.* y data or the superconductivity response with the nominal Cu content of the samples strongly suggest the existence of a small range of Cu non-stoichiometry in the compound $Nd_{1.85}Ce_{0.15}Cu_{1+\delta}O_y$. A Cu defect con-

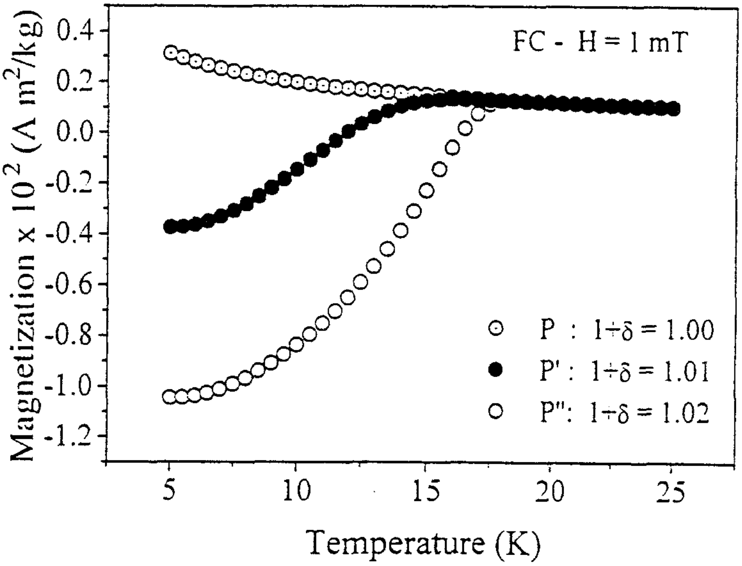


Fig. 5 SQUID signal, 1 mT field cooled d.c. magnetization, as a function of the temperature for $Nd_{1.85}Ce_{0.15}Cu_{1+\delta}O_y$ with $1+\delta$ values of 1.00, 1.01 and 1.02 after quenching from P_{O_2} and y values of points P, P′ and P″ indicated in Fig. 4

centration of ~1% in the Cu–O_2 layers means a characteristic distance between them of approximately 4 nm. As the coherence length of $Nd_{1.85}Ce_{0.15}CuO_y$ is $\xi_{||}$~8 nm [25], this defect would affect the superconducting response of the samples critically.

The possible Cu non-stoichiometry in the T′ phase of $Nd_{1.85}Ce_{0.15}Cu_xO_y$ ($0.94 \leq x \leq 1.06$) was studied by Cava *et al.* [26]. They explored the possibility of Cu non-stoichiometry on the basis of two ideas: Cu vacancies and substitution of Cu for Nd. However, from their high-intensity powder X-ray diffraction data, they concluded that the T′ structure does not display significant metal atom non-stoichiometry within their experimental uncertainty of 1% in the Cu content. More recently, we have suggested that the quite different superconducting response of $Nd_{1.85}Ce_{0.15}Cu_{1\pm\delta}O_y$ for $1\pm\delta$ values ranging between 0.99 and 1.02 may be due to the presence of a very small concentration of defects in the cationic sublattice [15, 17].

In spite of the evidence of Cu non-stoichiometry in $Nd_{1.85}Ce_{0.15}Cu_{1+\delta}O_y$, indicated by the present thermodynamic and superconducting data, it is difficult to elucidate the nature of such Cu defects. This is mainly due to their small concentration. However, we will speculate about some possibilities:

i) Cu interstitial atoms may be located at the sites (1/2, 1/2, 0), considering only the effective ionic radii of O^{2-} and Cu^{2+} in square planar coordination [27] (see the T′ phase structure in Fig. 6). However, the Madelung potential calculated by the Ewald method [28] at the site (1/2, 1/2, 0) is ~+2.7 eV. This positive value is mainly due to the presence of Nd^{3+} at the sites (1/2, 1/2, 0.14), which makes the sites (1/2, 1/2, 0) energetically unfavourable. Further, Cu interstitial atoms would result in scattering centres for the charge carriers of the CuO_2 layers, increasing the normal state resistivity. Nevertheless, the electrical resistivity data as a function of temperature for $Nd_{1.85}Ce_{0.15}Cu_{1+\delta}O_y$ samples with $1.00 \leq 1+\delta \leq 1.03$ indicate that the resistivity decreases as $1+\delta$ increases from 1.00 to 1.01 [16].

ii) Cu vacancies seem to be a more admissible hypothesis. Cava *et al.* [26] pointed out that the T′ structure might be able to accommodate a Cu deficiency and remain stable on account of the good three-dimensional interconnection of the Nd–O array. Thus, if the presence of Cu vacancies in sample 1.00 is assumed, it is plausible to expect that the resistivity decreases as the Cu content of the T′ phase is increased.

iii) A small substitution of Cu for Nd preserving site-balancing may also be possible, as observed in the pyrochlore structure for $Nd_{2-x}Cu_xRu_2O_{7-y}$ [29].

In sample 1.00, Cu vacancies should coexist with traces of free CuO in order to preserve the nominal Cu stoichiometry. However, sample 1.00 did not show the presence of free CuO, either by DTA or through SEM observations [17]. This may be due to a systematic error in the Cu content of the samples or to the occurrence of a small substitution of Cu for Nd. Therefore, in addition to the existence of Cu vacancies in sample 1.00, substitution of Cu for Nd in a concentration similar to that of Cu vacancies may also be possible. However, the small concentration of such defects (lower than 1% of the Cu sites of the CuO_2 layers) hampers its confirmation by other experimental techniques, such as X-ray diffraction or electron microscopy.

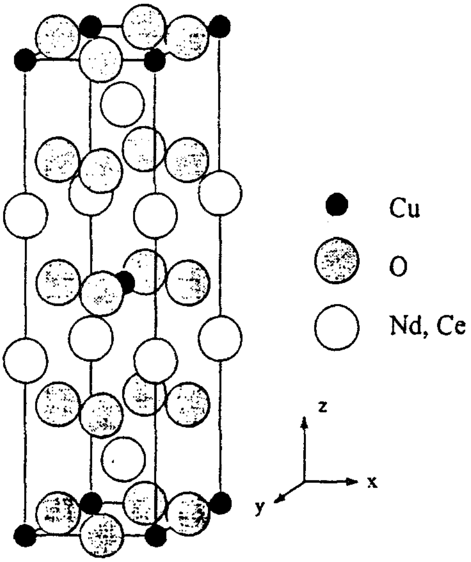


Fig. 6 Unit cell of the T′ structure

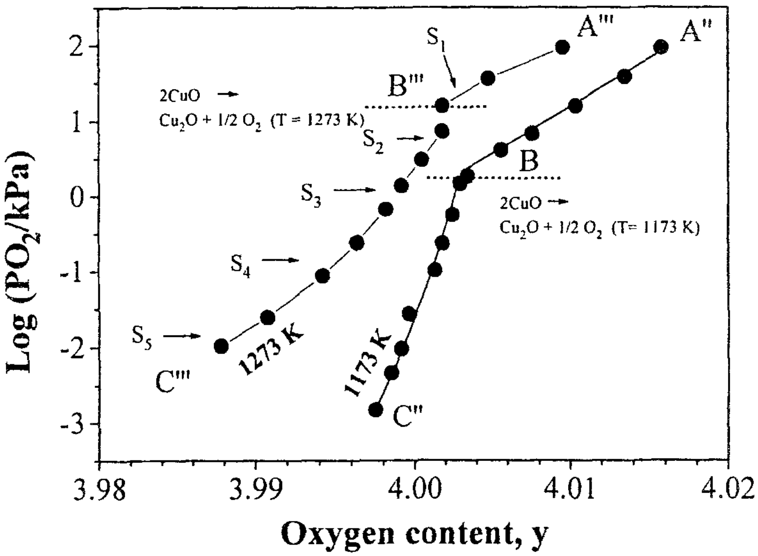


Fig. 7 log P_{O_2} as a function of y at 1173 and 1273 K for $Nd_{1.85}Ce_{0.15}Cu_{1.02}O_y$. Samples prepared with controlled oxygen contents are indicated by points S_1, S_2, S_3, S_4 and S_5

If the existence of Cu vacancies in the Cu–O_2 layers is assumed, as the more probable defects (with one or two effective negative charges), the bonding energy of neighbouring oxygen atoms should decrease through Coulombic repulsion. Therefore, at lower P_{O_2} values, the oxygen non-stoichiometry of sample 1.00 should be higher than those of 1.01 and 1.02 ($\Delta y_{BC} > \Delta y_{BC'} > \Delta y_{BC''}$). At higher P_{O_2} (parts A–B, A′–B and A″–B), the larger oxygen contents of samples 1.01 and 1.02 may be explained basis of the on the electroneutrality condition. Higher Cu contents in samples 1.01 and 1.02 require higher oxygen contents. However, the explanation for the intersection of the three curves at point B, which corresponds to the Cu_2O–CuO equilibrium, is not evident. Nevertheless, this point plays a critical role in the reduction step [7, 13], as will be discussed later.

In order to study the relation between oxygen content and superconductivity in $Nd_{1.85}Ce_{0.15}Cu_{1+\delta}O_y$, we measure the dc magnetization response of samples 1.02 with controlled oxygen contents. Figure 7 displays the $\log P_{O_2}$ *vs.* y data for sample 1.02 at 1173 and 1273 K after correction for the CuO–Cu_2O phase transition. The 1273 K isotherm exhibits behaviour similar to that at 1273 K. Once again, the curve obtained at 1173 K has two well differentiated parts at $\log(P_{O_2}/\text{kPa}) \approx 1.1$, which corresponds to the CuO–Cu_2O equilibrium. At P_{O_2} levels higher than this value, the oxygen contents are higher than 4.00, and at P_{O_2} levels lower than this value, the oxygen contents are lower than 4.00. Measurements of the kinetic evolution towards equilibrium after step change in P_{O_2} performed at 1173 K above and below the P_{O_2} corresponding to the CuO–Cu_2O equilibrium suggested two kinds of oxygen defects: interstitial oxygen atoms for P_{O_2} higher than this value, and oxygen vacancies for P_{O_2} lower than the CuO–Cu_2O equilibrium [13]. The oxygen non-stoichiometry in part B‴C‴ of the 1273 K isotherm, corresponding to the creation of oxygen vacancies, is larger than that in part BC″ of the 1173 K isotherm. Therefore, in order to prepare samples with larger oxygen content variations, the annealing treatment was performed at 1273 K. The samples with controlled oxygen con-

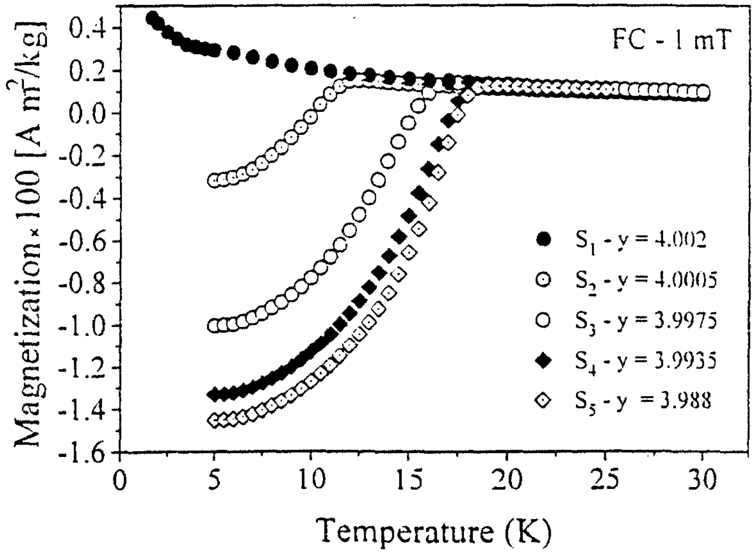


Fig. 8 SQUID signal, 1 mT field cooled d.c. magnetization, as a function of the temperature of $Nd_{1.85}Ce_{0.15}Cu_{1.02}O_y$ after quenching from P_{O_2} and y values of points S_1, S_2, S_3, S_4 and S_5 indicated in Fig. 7

tents were prepared by annealing at temperature and P_{O_2} values corresponding to the points S_1, S_2, S_3, S_4 and S_5 in the 1273 K isotherm in Fig. 7. Figure 8 depicts the SQUID signal as a function of temperature in 1 mT field cooled runnings. As reported previously [7, 13], superconductivity is achieved only in samples prepared under a P_{O_2} lower than that of the CuO–Cu_2O equilibrium at 1173 K. The lack of superconductivity of the S_1 sample was verified down to 1.7 K.

Figure 9a plots T_c, and Fig. 9b the Meissner (FC) and shielding (ZFC) fractions under a field of 1 mT, measured at 5 K as a function of the oxygen content y of the T′ phase. T_c and the Meissner and shielding fractions are initially zero and then increase as the oxygen content decreases below the critical value of 4.00.

The nature and concentration of the oxygen defects critically affect the superconducting response of $Nd_{1.85}Ce_{0.15}Cu_{1.02}O_y$. The presence of a small amount of interstitial oxygen atoms (y>4.00) makes it impossible to achieve superconductivity, while the superconducting response is improved as the concentration of oxygen vacancies (y) increases.

To summarize, our measurements of the equilibrium P_{O_2} as a function of the oxygen content y in samples of $Nd_{1.85}Ce_{0.15}Cu_{1+\delta}O_y$ show a dependence of the oxygen non-stoichiometry on the nominal Cu content ($1+\delta=1.00$, 1.01 and 1.02). Furthermore, the superconducting response is depressed for samples with stoichiometric nominal Cu contents in spite of the larger oxygen non-stoichiometry. These facts have been discussed in terms of the existence of Cu non-stoichiometry in the T′ phase. We propose that the Cu non-stoichiometry in sample 1.00 is associated with Cu vacancies in the CuO_2 layers with a concentration of ~1% on the Cu sites.

Moreover, superconductivity suddenly appears in samples of $Nd_{1.85}Ce_{0.15}Cu_{1.02}O_y$ obtained at P_{O_2} just below the CuO–Cu_2O equilibrium at 1273 K. This last observation was previously reported by Kim *et al.* [7] and later confirmed [13] for a sample with a nominal Cu content $1+\delta=1.01$.

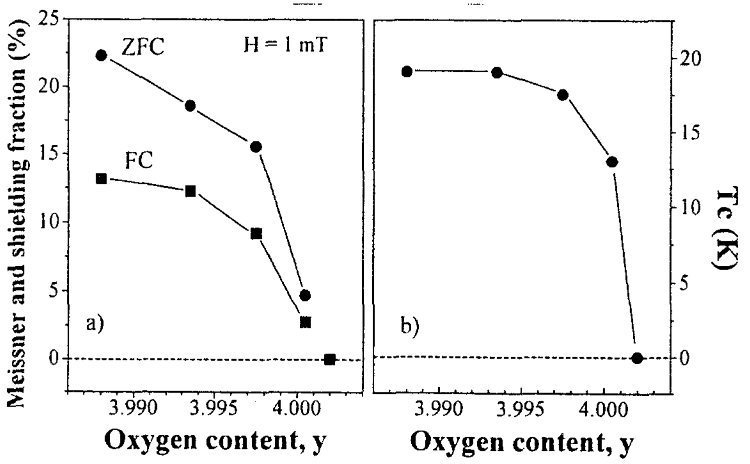


Fig. 9 Superconducting response of $Nd_{1.85}Ce_{0.15}Cu_{1.02}O_y$. T_c as a function of the oxygen content y (a) and Meissner and shielding fractions as a function of the oxygen content y at 5 K (b)

Measurements of the conductivity as a function of the equilibrium P_{O_2} at high temperature are in progress in order to clarify the role of the reduction step in $Nd_{1.85}Ce_{0.15}Cu_{1+\delta}O_y$.

* * *

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