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Oxygen content influence in the superconducting and electronic properties of $Nd_{1.85}Ce_{0.15}Cu_{1.01}O_y$ ceramics

E. Navarro[a,*], D. Jaque[b], J.E. Villegas[b], J.I. Martín[b], A. Serquis[c], F. Prado[c], A. Caneiro[c], J.L. Vicent[b]

[a]*Departamento Física Aplicada, Facultad de Veterinaria, Universidad Complutense, 28040 Madrid, Spain*
[b]*Departamento Física de Materiales, C.C. Físicas, Universidad Complutense, 28040 Madrid, Spain*
[c]*Instituto Balseiro y Centro Atómico Bariloche, CNEA, 8400 S.C. de Bariloche, Argentina*

Abstract

Superconducting and electronic properties of $Nd_{1.85}Ce_{0.15}Cu_{1.01}O_y$ ceramic samples have been studied as a function of the oxygen content. It has been observed that values of oxygen content 'y' above those corresponding to the CuO–Cu_2O equilibrium partial oxygen pressure destroy superconductivity. On the other hand, for lower oxygen contents, resistivity and magnetic superconducting transitions are present with critical temperature values up to 20 K. The normal state Hall effect has also been measured presenting a negative R_H coefficient in all the samples. For superconducting samples, R_H is not significantly dependent on the oxygen content value. In addition, the Hall coefficient is almost temperature independent in these samples. It is in contrast with some of the non-superconducting samples where the absolute value of R_H increases as T decreases. These results reveal that, for samples obtained by annealing below the CuO–Cu_2O equilibrium partial oxygen pressure, the enhancement of superconducting properties as oxygen is reduced is not produced by a change in the carrier density, pointing then to a structural ordering effect as an explanation.

Keywords: Superconductors; Chemical synthesis; Point defects; Electronic transport; Magnetisation

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1. Introduction

The role of oxygen has been an important topic in cuprate superconductors. In many hole-doped cuprates, superconductivity can be induced by either cation or oxygen doping because oxygen strongly affects the carrier density and the critical temperature, T_C.

The $Ln_{2-x}(Ce,Th)_xCuO_y$ (Ln=Nd, Pr, Sm and Eu) are one of the most interesting families of the superconducting cuprates [1]. They present the simplest crystal structure, the so-called T′ tetragonal phase. The electron doping like behavior in their transport properties makes them suitable for comparison with the hole-doped cuprates families. From this comparition, the influence of the carrier type on the superconducting properties can be studied.

One of the main features of this system is the extreme sensitivity of its superconducting response to small variations in the doped content (Ce, Th) and oxygen content 'y'. In this way, changes in the Ce concentration 'x' can induce a sign reversal from negative to positive in the normal state Hall coefficient R_H [2–5]. Moreover, the sign can be reversed by reducing the temperature [6,7]. Also, oxygenation and reduction in vacuum processes can induce a change in the sign of the Hall coefficient [3,6]. It is evident that oxygen atoms are removed during the reduction step. The question concerning which are the oxygen crystal sites involved in this process seems to be clear. It is now accepted that interstitial oxygen atoms located at the apical sites of the T′ structure are removed during this treatment. However, the amount of oxygen removed is very small, with values ranging between 0.01 and 0.05 per unit formula [8,9]. This amount seems to be too small to explain the induction of superconductivity as due to a variation on the carrier concentration.

Moreover, it has been reported for $Nd_{1.85}Ce_{0.15}Cu_{1.01}O_y$ that superconductivity appears suddenly in samples quenched at $p(O_2)$ just below the CuO–Cu_2O equilibrium [10–12]. If the interstitial oxygen atoms were the cause of the absence of superconductivity, this should be induced progressively as the concentration of interstitial oxygen atoms decreases in the sample. Nevertheless, the sudden appearance of superconductivity for samples prepared under a $p(O_2)$ just below the line corresponding to the

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*Corresponding author. Tel.: +34-91-394-4558 extn. 4548.
E-mail address: enavarro@eucmos.sim.ucm.es (E. Navarro).

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CuO–Cu_2O equilibrium might also suggest that another process could be present for inducing superconductivity.

Hall effect measurements in samples with homogeneous cerium concentration and an accurate controlled oxygen content could provide an important clue to the elucidation of the mechanism of high-temperature supercondutor behavior of this compound.

In this paper we report on both resistance and Hall measurements in the temperature range from 200 to 7 K. This results are compared with the magnetic measurements of the Meissner effect. Measurements have been carried out on $Nd_{1.85}Ce_{0.15}Cu_{1.01}O_y$ samples with different oxygen content 'y'. These experiments allowed us to discuss the nature of defects and their influence in the superconducting response.

2. Experimental

The synthesis of $Nd_{1.85}Ce_{0.15}Cu_{1.01}O_y$ with accurately controlled Cu content was carried out by the liquid mix method (LMM). The LMM has been previously described in the literature [13]. The advantage of this method is that they provide samples with a better Ce distribution that the common solid state reaction method.

Equilibrium $p(O_2)$ measurements were performed using thermogravimetric equipment consisting of a symmetrical thermobalance based on a Cahn 1000 electrobalance coupled to an electrochemical system to measuring and controlling $p(O_2)$ [14]. The absolute oxygen content of the samples was determined thermogravimetrically in situ by reduction in dry H_2 at 1100°C after all the mass variation measurements were completed, assuming Nd_2O_3, Ce_2O_3 and Cu as reduction products. Oxygen content has been varied by annealing at 900°C under different oxygen partial pressure $p(O_2)$ and subsequent quenching to liquid nitrogen [15]. It should be noted here that our thermogravimetric equipment allowed us to detect changes in the oxygen content 'y' within 3×10^{-4} for a sample of about 7 g of $Nd_{1.85}Ce_{0.15}Cu_{1.01}O_y$.

The transport characterization has been done in a commercial helium cryostat with a superconducting solenoid of 9 T. The standard four-point set up was used to simultaneously recording voltage and current. The sample was placed into the cryostat in such a way that the magnetic field was always applied perpendicular to the transport current. The samples have been prepared into 250 μm thick pellets in order to perform Hall effect measurements. Dc magnetization were performed with a Quantum Design SQUID magnetometer.

3. Results and discussion

In Fig. 1 are plotted the equilibrium $p(O_2)$ measurements as a function of oxygen content 'y' for the $Nd_{1.85}Ce_{0.15}Cu_{1.01}O_y$ samples. A clear change in the slope of this curve is observed at the $p(O_2)$ corresponding to the CuO–Cu_2O equilibrium.

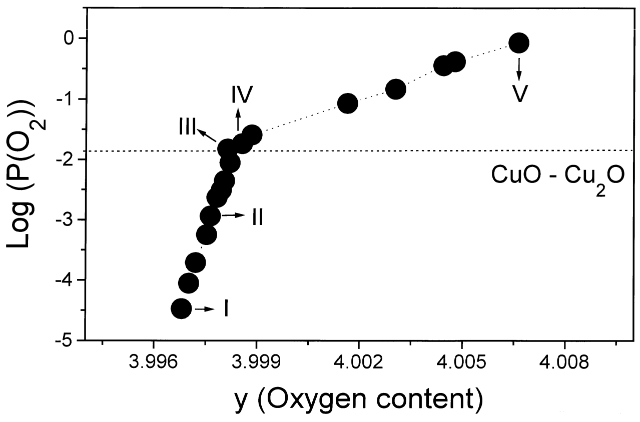

Fig. 1. Equilibrium oxygen partial pressure $p(O_2)$ as a function of oxygen content 'y' for $Nd_{1.85}Ce_{0.15}Cu_{1.01}O_y$ at 900°C.

Fig. 2 shows the Meissner fraction (field cool measurements) dependence with the temperature for $Nd_{1.85}Ce_{0.15}Cu_{1.01}O_y$. The samples were prepared with accurate control of the oxygen content by annealing them for 24 h at 900°C under $p(O_2)$ values corresponding to points indicated in Fig. 1 and subsequent quenching to liquid nitrogen. A very important fact observed is the lack of superconductivity for samples quenched from $p(O_2)$ where CuO is stable over Cu_2O (points IV and V). The superconductivity appears suddenly for samples quenched from $p(O_2)$ values where Cu_2O is stable over CuO. Samples I and II show a diamagnetic signal at $T_C\approx20$ and 17 K, respectively, whereas sample III shows a smaller (but non vanishing) diamagnetic signal at 13 K. This experimental evidence has been already reported by Kim et al. [11] and Prado et al. [10,12].

For $p(O_2)$ values higher than the values which correspond to the CuO–Cu_2O equilibrium interstitial oxygen

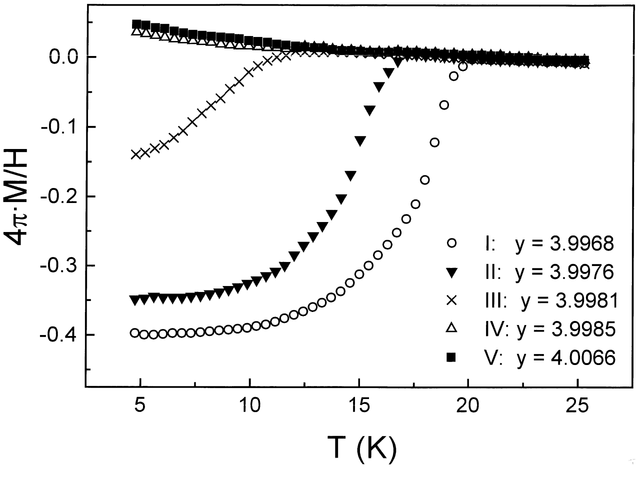

Fig. 2. Meissner fraction for samples prepared after quenching from $p(O_2)$ and 'y' values of points I, II, III, IV and V in Fig. 1.

excess should be present located in the apical site of the T′ structure of the sample. For p(O_2) values lower than that of the CuO–Cu_2O equilibrium, the thermodynamic data indicate oxygen deficiency.

Fig. 3 shows the thermal dependence of the resistance for three different samples. Samples I (y=3.9968<CuO–Cu_2O equilibrium) and II (y=3.9976<CuO–Cu_2O equilibrium) have resistivity superconducting transitions, with a T_C according to Meissner effect measurements (see Fig. 2). A different behavior is exhibited by sample III (y=3.9981>CuO–Cu_2O equilibrium), which have a superconducting onset at a reduced temperature. As for the diamagnetic signal, superconductivity behavior is not totally suppressed (a reduction in resistance at 13 K can be observed from Fig. 3). This can be tentatively explained in terms of non homogeneous sample, in such a way that superconductivity remains in some extensions in the sample. Sample IV (y=3.9985>CuO–Cu_2O equilibrium) shows similar temperature dependence as sample III. For sample IV reduction in resistance is also observed but at lower temperature than in sample III. Finally, sample V (y=4.0066>CuO–Cu_2O equilibrium) shows an insulator behavior. In fact, it shows resistance values much greater than superconducting samples. This increment of the resistance for the high oxygen content has been discussed in a previous publication [15] and it has been attributed to the presence of oxygen defect in the bulk material due to the oxygen concentration excess.

For the sake of clarity the temperatures below which Messiner effect takes place are plotted in Fig. 4 as a function of oxygen content.

Fig. 5 shows the Hall effect behavior found in several samples with different oxygen contents. All measured samples present negative values in the Hall resistivity. The Hall coefficients, R_H, for samples I, II and IV show an almost temperature independent behavior. Sample III, which presents a reduced diamagnetic signal, present higher R_H absolute value in comparison with the best superconducting samples in the low oxygen concentration range (I and II) and with sample IV. All measured samples show the typical linear dependence as a function of field [16]. R_H is almost independent on the oxygen content for the two superconducting sample (I and II) although the relative oxygen reduction has still improved the superconducting properties (samples I and II have a $T_C \approx 20$ and 17 K, respectively as can be observed from Figs. 2 and 3).

This Hall effect data indicate that for oxygen content y>3.998 the improvement in the superconducting properties as the oxygen concentration is reduced can be associated to a doping effect due to the decrease in the interstitial oxygen atoms. However, for y<3.998, since R_H is independent of y, our results suggest that the free carries

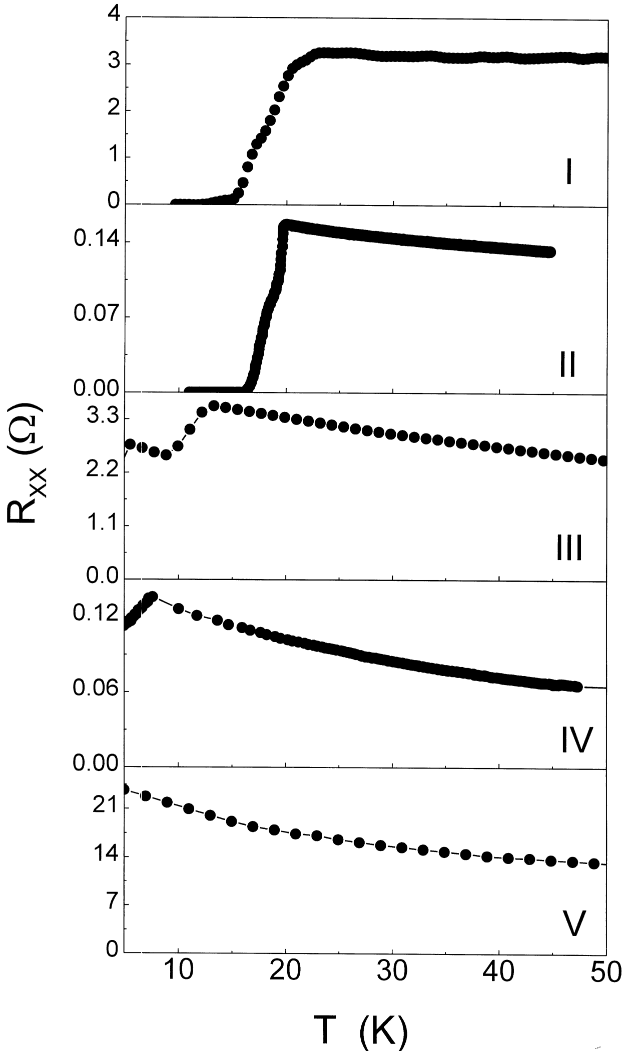

Fig. 3. Thermal dependence of the resistance for samples with different oxygen content.

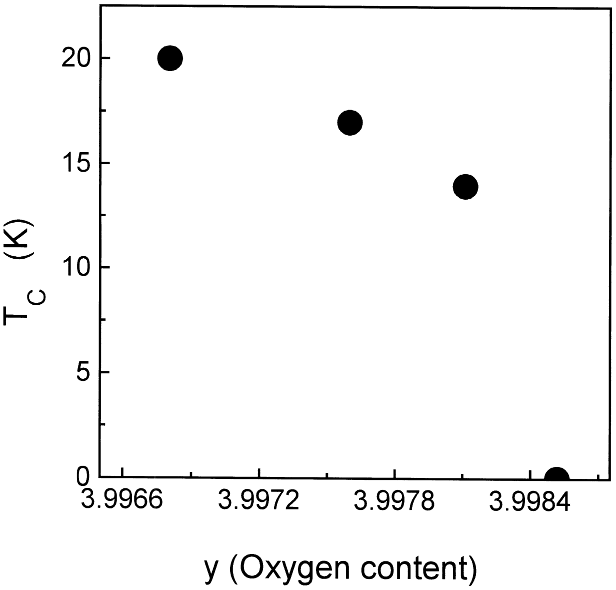

Fig. 4. The temperatures below which Meissner effect takes place as a function of oxygen content.

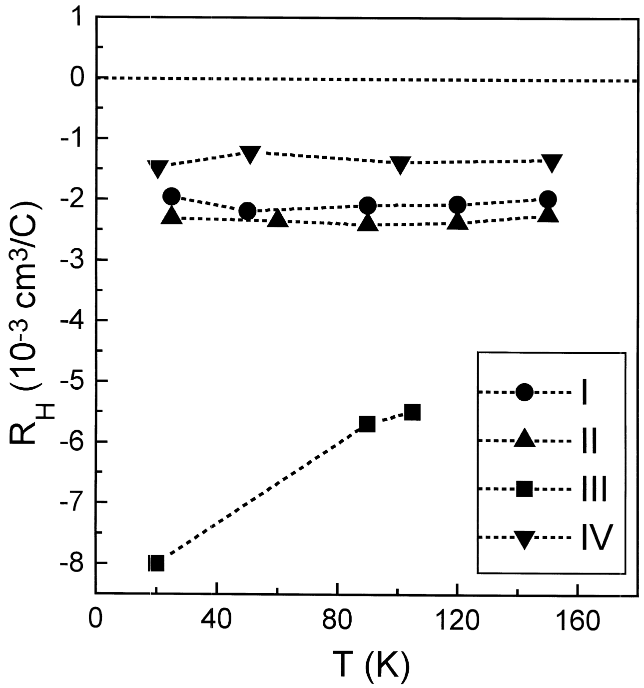

Fig. 5. Temperature dependence of Hall coefficient for samples with different oxygen content.

come from Ce doping, and that the improvement in T_C is not due to the oxygen doping but rather to the structural effect of reducing microstrains. This is good agreement with previous results [15], that show the conductivity value is also independent of oxygen concentration in this '*y*' range where superconducting properties are optimized.

4. Conclusion

The superconductor behavior has been attributed to a reduction of the interstitial oxygen atoms when '*y*' is decreased down to $y=3.998$ and then, when '*y*' is further reduced, to a relief in the microstrains due to the CuO–Cu_2O transformation [15]. For p(O_2) values higher than that corresponding to the CuO–Cu_2O equilibrium interstitial oxygen excess should be present located in the apical site of the T′ structure of the sample. For p(O_2) values lower than that of the CuO–Cu_2O equilibrium, the thermodynamic data indicate oxygen deficiency. As far as the R_H coefficients determine no dependence of the carrier concentration on the oxygen content, superconducting or insulator behavior can be only related to structural features. The thermal dependence of the resistance also point to structural inhomogeneities induced by high oxygen content.

Acknowledgements

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