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Oxygen distribution in $La_{1.8}Sr_{0.2}CuO_{4-\delta}$: Effects on transport properties

R. Decca, D. Serafini, F. de la Cruz, and J. Abriata
Centro Atómico Bariloche and Instituto Balseiro, 8400 San Carlos de Bariloche, Río Negro, Argentina

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We determined the effect of oxygen depletion on transport properties of $La_{1.8}Sr_{0.2}CuO_{4-\delta}$ ceramic samples measuring simultaneously the change of resistivity and mass as a function of oxygen partial pressure, at 900 °C. It has been found that the sample resistance is extremely sensitive to small changes of the sample oxygen content, indicating that oxygen vacancies are highly correlated. The results support a granular picture where quasiparticles in the normal state and electron pairs in the superconducting state tunnel through insulating barriers. In this picture oxygen occupies two well distinguishable regions in the sample: one associated to the intragrain superconducting material and the other to the intergrain weak links. We show that the interpretation of conventional techniques used to determine the absolute value of the oxygen content does not produce meaningful results.

I. INTRODUCTION

It is well known that the superconducting and normal properties of the copper oxide superconductors are strongly determined by the oxygen content of the material. Although the effect of oxygen concentration has been extensively studied in most of the high-temperature superconductors, the correlation between the change of its physical properties and the change of oxygen concentration is often made[1–3] assuming that the oxygen depletion is homogeneous throughout the sample. On the other hand preliminary simultaneous measurements[4] of the electrical resistivity and the weight of oxygen in ceramic samples of $La_{1.8}Sr_{0.2}CuO_{4-\delta}$ have shown that oxygen depletion introduces two well-distinguishable scattering mechanisms in the resistivity: one associated to tunneling of quasiparticles from grain to grain and another due to electron-oxygen vacancy scattering in the bulk of the grain. These data allow the introduction of a unified picture where granularity is shown to be responsible for the main characteristics of the superconducting as well as the normal electrical transport properties. It explains why the electrical resistance of the normal state can be discussed in terms of a single homogeneous electronic system[5,6] with different electron scattering mechanisms rather than in terms of electrical conduction of intra- and intergrain materials with different conductivities.

Experiments where oxygen plays an important role are those made to determine the electrical resistivity in the normal state. In these cases the oxygen depletion induces a change in regime of the electrical resistivity, which shows[2,5,6] a metallic behavior at high temperatures and a localized variable range hopping regime at low temperatures. In principle, the change in regime depends on the disorder associated to oxygen vacancies, the change of carrier concentration, or both.

High-temperature resistivity measurements in La-Sr-Cu-O as a function of oxygen and strontium content have been interpreted[5,7] assuming that while the strontium content modifies the number of carriers, it remains essentially constant under the variation of oxygen content, induced in those experiments. As a consequence, the change in regime of the resistive behavior as well as the variation of its absolute value should be related to the disorder induced by oxygen vacancies. On the other hand, this result seems to be in contradiction with the assumption[3] that the density of carriers p is proportional to $x-2\delta$, where x is the Sr concentration. In this picture x and δ play an equivalent role in determining the carrier concentration.

A large amount of experimental and theoretical work shows that ceramic superconductors are ideal systems[8,9] to study the response of superconducting disordered networks. The H-T phase diagram as well as the description of the critical state of the whole system can be described using properly renormalized[8,10,11] superconducting parameters in the first case and a modified[12] Bean's critical model[13] in the second one. However, the broadening[14] of the superconducting transition in the La-Sr-Cu-O compound, as well as in other ceramic compounds[15], has been shown to be essentially determined by the fluctuation of the phase of the order parameter nucleated in different superconducting grains. The coupling between different grains of the La-Sr-Cu-O ceramics is made through weak junctions that can be tuned[5,8,14] controlling the oxygen content in the sample. On the other hand the slope, $\frac{dR}{dT}$, of the temperature dependent resistance in the normal state is not modified[4,6,16] by those changes of the oxygen concentration, indicating that the variation of the intergrain coupling should not be related to a change in the carrier density.

An important characteristic of the $La_{1.8}Sr_{0.2}CuO_{4-\delta}$ system that was made evident[17] by the measurement of the equilibrium partial pressure of oxygen is its tendency to show a well-defined plateau as a function of oxygen content which is indicative of phase segregation. In most cases the amount of phase segregated is so small that it is undetectable by conventional x-ray diffraction analysis. Nevertheless, precise oxygen partial pressure

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P_{O_2} measurements allowed us to demonstrate[17] that the second phase in $La_{1.8}Sr_{0.2}CuO_{4-\delta}$ is $La_{6.25}Sr_{1.75}Cu_8O_{20}$ (an oxygen-deficient, perovskite-type structure) which decomposes below 10^{-2} atm. This result might suggest that the origin of granularity in the La-Sr-Cu-O system could be caused by the segregation of small amounts of this impurity phase separating the superconducting regions. However, this implies a specific topology of the segregated phase which is difficult to justify.

The scope of this work is oriented to investigate the behavior of the electrical resistance of the $La_{1.8}Sr_{0.2}CuO_{4-\delta}$ ceramic as a function of the equilibrium oxygen partial pressure as well as the changes induced in the transport properties by a non-equilibrium oxygen content. The results allow one to elucidate the influence of the oxygen spatial distribution in the normal and superconducting properties of those ceramics.

The simultaneous measurement of the electrical resistivity and the change of weight due to the variation of the oxygen concentration show that the experimental data are consistent with a granular picture, where quasiparticles and superconducting pairs tunnel between metallic islands through thin insulating barriers.

II. SAMPLE PREPARATION AND EXPERIMENTAL TECHNIQUES

Samples were prepared using the citrate precursors method.[18] We used La_2O_3, copper (as copper nitrate, in solution), and $SrCO_3$ as precursors. La_2O_3 was thermogravimetrically analyzed in order to assess the quantity of water[19] adsorbed and chemically bonded as $La(OH)_3$.

The powder obtained was pressed and sintered for 24 h at 1040 °C. X-ray analysis of samples gave a spectrum characteristic of single-phase $La_{1.8}Sr_{0.2}CuO_{4-\delta}$.

The construction, details, and performance of the experimental equipment used in our thermogravimetric measurements were described[20] in detail elsewhere. In essence, this equipment consists of a symmetrical Cahn 1000 electrobalance coupled to an electrochemical system (pump and oxygen gauge) for the measurement and regulation of P_{O_2}. Weight changes can be measured within $\pm 5 \times 10^{-6}$ g, so it was possible to determine changes in δ within $\pm 2 \times 10^{-4}$, for our samples of about 1 g of $La_{1.8}Sr_{0.2}CuO_{4-\delta}$. The appropriate oxygen atmosphere was obtained by a mixture of argon-oxygen, supplied by the electrochemical system, with P_{O_2} values ranging from 10^{-6} atm to 1 atm. Estimated errors in P_{O_2} were $\pm$ 2%.

In order to make the experiments we cut several slabs of $10 \times 2 \times 0.25$ mm^3. We attached four contacts in one of them, $S1$, which was located just below the crucible of the thermobalance, where the other slabs were weighted. The temperature difference between the crucible and $S1$ was maintained below 0.5 K. We measured the electrical resistance using a conventional lock-in technique at a frequency $\nu = 137$ Hz and a current of 1 mA. The sensitivity in the resistance was better than 0.05 mΩ.

The measurement of the electrical resistance and sample weight was made in and out thermodynamic equilibrium. We defined the thermodynamic equilibrium state as that when the weight of the sample changes in less than 20 μg per h and the corresponding resistance in less than 0.1 mΩ per h. The equilibrium in weight and resistance were obtained simultaneously. Once it was reached P_{O_2} was changed and the resistance and weight were plotted as a function of time. The typical changes in P_{O_2} were of the order of $\frac{\Delta P}{P} = 0.5$. P_{O_2} as measured by the electrochemical cell was stabilized in time orders of magnitude shorter than the oxygen diffusion time of the sample.

III. RESULTS AND DISCUSSION

Figure 1 shows the resistivity of the sample investigated, after full oxygenation at 900 °C. The results reproduce those observed in many other experiments[4,6,16] and can be taken as representative of the behavior of the ceramic samples.

Figure 2(a) shows the relative change of mass $\frac{\Delta m}{m_0}$ as a function of the equilibrium P_{O_2}, where $m_0 = 0.985\,53$ g is the equilibrium total mass of the sample at a $P_{O_2} = 1$ atm and $\Delta m = m_0 - m$. The decomposition plateau is evident at a pressure $P \simeq 10^{-2}$ atm, in agreement with previous results[17]. The amount of the impurity phase is estimated to be less than 3% in weight.

In Fig. 2(b) we have plotted the electrical resistivity as a function of the corresponding equilibrium P_{O_2}.

The data of Fig. 2 show that the impurity phase decomposition has no detectable effect in the resistivity. This was also verified measuring the normal state resistivity and the superconducting transport properties as a function of field and temperature of different samples, where the extension of the plateau as a function of $\frac{\Delta m}{m_0}$ varied in 1 order of magnitude. Neither the superconducting granularity nor the normal state resistivity were modified by the presence of the impurity phase.

The results shown in Fig. 2 indicate that the small amount of impurity phase is concentrated in isolated regions distributed within the sample, making no measurable contribution to the transport properties of the

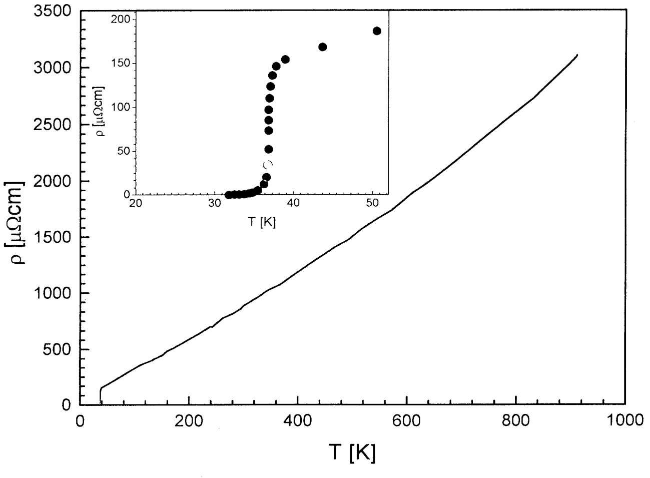

FIG. 1. Resistivity as a function of temperature for a fully oxygenated sample. The sample was oxygenated at 900 °C in $P_{O_2} = 1$ atm. The inset shows details of the superconducting transition.

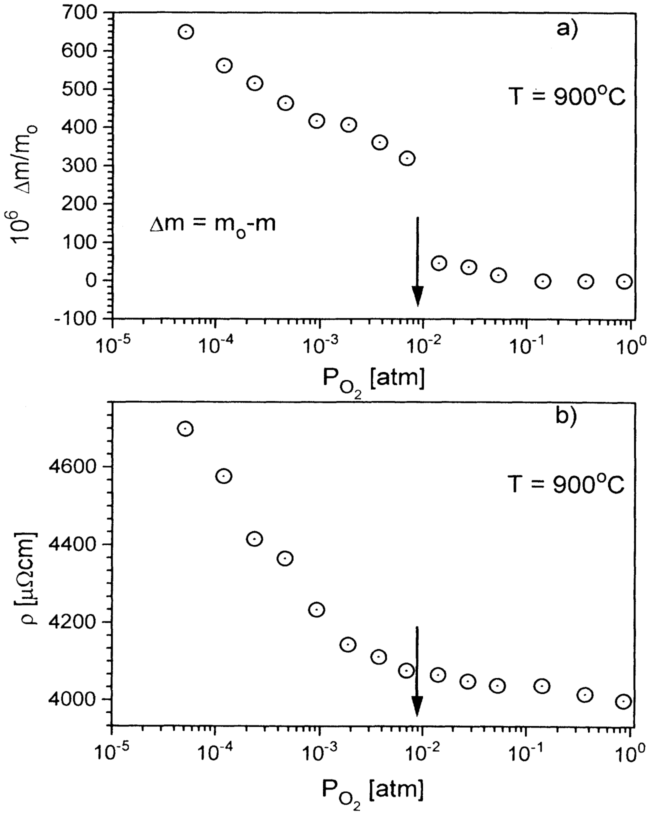

FIG. 2. (a) Relative change of mass $\frac{\Delta m}{m_0}$ as a function of oxygen partial pressure P_{O_2}. $m_0 = 0.985\,53$ g is the mass of the fully oxygenated state. (b) Resistivity as a function of P_{O_2}. In each case the arrow indicates the particular P_{O_2} at which $La_{6.25}Sr_{1.75}Cu_8O_{20}$ decomposes (see text). The measurements are in thermodynamic equilibrium.

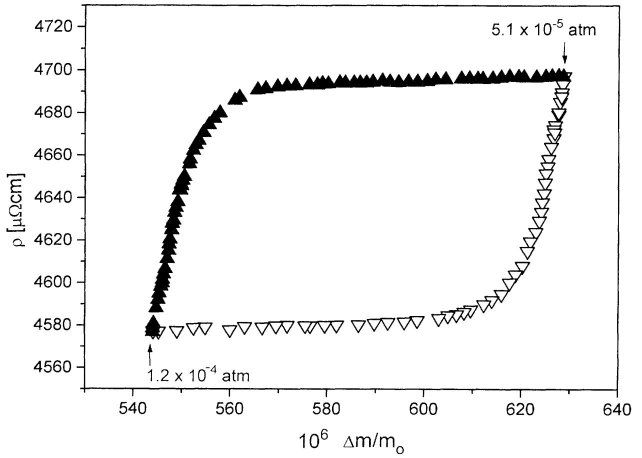

FIG. 3. Hysteretic behavior of the resistivity as a function of relative change of mass $\frac{\Delta m}{m_0}$. These measurements are out of thermodynamic equilibrium. The arrows indicate the initial and final equilibrium P_{O_2}.

majority phase. As a consequence these results provide clear evidence that the granularity of the superconducting state is unrelated to the existence of the thermogravimetrically observed second phase segregation.

Figure 3 shows the hysteretic relation between resistivity and mass, induced by a sudden change of pressure from the initial equilibrium state at $P_1 = 1.2 \times 10^{-4}$ atm to $P_2 = 5.6 \times 10^{-5}$ atm and then (after the new equilibrium state is reached) back to P_1. The equilibrium states are indicated by the arrows, with the corresponding P_{O_2}. In both cases the change in pressure was made and stabilized in less than 1 min while the equilibrium state in the sample was reached in about 5 h. The results in this figure are representative of the behavior found in the whole range of partial pressures investigated, from $P_{O_2} = 1$ atm to $P_{O_2} = 10^{-5}$ atm.

The results plotted in Fig. 3 are rather surprising. The resistivity is found to be very sensitive to small changes of oxygen content, once the mass starts to vary after the sudden change in pressure. This occurs either under oxidation or reduction. When approaching the new equilibrium state the slope $\frac{dR}{dm}$ is reduced by a factor of the order of 100. This means that just after the partial pressure is modified a very small amount of change in mass induces a large variation of the resistivity, while at longer periods of time the mass has to change 100 times more to produce an equivalent change of resistance.

It has been previously shown[6,16] that the absolute value of the resistance could be changed by more than 1 order of magnitude at low temperatures, while the derivative of the resistance at high temperature $\frac{dR}{dT}$ remained constant. In these experiments oxygen is removed or added at high temperature and then the sample is cooled to some lower temperature where the oxygen mobility is essentially zero. The fact that $\frac{dR}{dT}$ remains constant for different oxygen contents has also been checked in this paper. In this work $\frac{dR}{dT}$ was determined for samples in thermodynamic equilibrium at a given partial pressure, as well as at different stages of the evolution of the sample toward that equilibrium. In all cases $\frac{dR}{dT}$ remained constant and equal in absolute value to that of Fig. 1, within an experimental error of less than 3%. These experiments were made changing the oxygen partial pressure at 900 °C, then the sample kept at that temperature for periods ranging from minutes to hours before cooling. As a consequence, the data show that the diffusion time at a sample dimensions scale is much shorter than the typical time involved in the process of cooling. The constancy of $\frac{dR}{dT}$ is also a strong indication that the change of resistance should not be related to a change of the effective geometrical factor of the sample.

Let us discuss the resistance measurements within the simple Drude model. In this model the resistance is

$$R = \rho\frac{L}{A} = \frac{m_e}{pe^2\tau}\frac{L}{A}\ , \tag{1}$$

where L and A are the length and area of the sample, m_e is the effective electronic mass, and τ is the relaxation time. The electrical resistivity at high temperatures and constant oxygen content has been shown[6,16] to follow a metallic behavior well represented by

$$\rho(T) = \sigma^{-1}(T) = \frac{m_e}{pe^2}\left(\frac{1}{\tau_e} + \frac{1}{\tau_i}\right) , \qquad (2)$$

where τ_e and $\tau_i \propto T^{-1}$ are the elastic and inelastic relaxation times, respectively. In this case the T^{-1} dependence closely represents the experimental behavior of the resistivity. The variation of oxygen content is expected to change the electrical resistivity through two different processes. One due to the change of the number of carriers, $\Delta p \propto \Delta m$, not observed[4,6,16] experimentally (as discussed in the Introduction). The second is the change[14] induced in τ_e by the disorder associated to oxygen vacancies. If anyone or both of the expected contributions were to be due to a uniform change of oxygen content we expect a linear change $\frac{\Delta\sigma}{\sigma} \simeq \frac{\Delta m}{m}$, where σ and m represent the values at the initial equilibrium partial pressure. From the results of Figs. 2 and 3 it is seen that this is not the case. As a consequence, we conclude that in the nonequilibrium experiments the change in oxygen concentration is not uniform within the sample.

Considering that the oxygen concentration is varied changing the atmosphere oxygen partial pressure we could expect a gradient of concentration perpendicular to the sample surface. In this case expression (1) is not valid and the sample can be modeled as a parallel distribution of sheets of different conductivities, with a sample conductance given by

$$\Sigma = \frac{1}{R_{\text{eff}}} = \frac{W}{L}\int_{-D/2}^{D/2} \sigma(y)dy , \qquad (3)$$

where W is the width of the sample, D is the thickness, and $\sigma(y)$ represents the conductivity associated to a local oxygen distribution. Although the function $\sigma(y)$ is unknown, there are several considerations that can be made to visualize the expected qualitative behavior that R_{eff} should show as a function of Δm.

The total variation of $\sigma(y)$ is bounded between the equilibrium value before changing the oxygen partial pressure and that corresponding to the final pressure. Since in the experiments these changes are small, see Fig. 3, we expect $\frac{\Delta\sigma(y)}{\sigma} \simeq \frac{\Delta\rho(y)}{\rho} \simeq \frac{\Delta m(y)}{m}$. Under this reasonable assumption the integration of expression (3) shows that the change of conductance should be proportional to the change of mass, $\frac{\Delta\Sigma}{\Sigma} \simeq \frac{\Delta R}{R} \simeq \frac{\Delta m}{m}$.

The previous discussion shows that the results of Fig. 3 cannot be explained either by a uniform depletion of oxygen in the sample or by a gradient of oxygen inducing a laminar distribution with different conductivities. However, the analysis of the evolution of the resistance as a function of mass indicates a topological material distribution able to induce strong variations of the electrical resistance with only small changes of the sample oxygen content.

To get an insight of the effect of oxygen vacancies in the transport properties, let us estimate the scattering cross section of the oxygen defects σ_{eff} at the beginning of the evolution towards equilibrium, in experiments as those shown in Fig. 3. If we assume that the oxygen vacancies are uncorrelated and distributed uniformly in the sample, the calculation can be done using the expression[21]

$$\Delta\rho = \frac{m_e v_f N_i \sigma_{\text{eff}}}{e^2} , \qquad (4)$$

where v_f is the Fermi velocity and N_i the density of defects. Taking a typical experimental slope at the start of oxygen depletion, $\frac{d\rho}{dm} = 15\frac{\Omega cm}{g}$ and using a free-electron gas picture, we obtain $\sigma_{\text{eff}} = 3000$ Å^2. When comparing this value to the average distance between vacancies of 25 Å it can be seen that the assumption of uniform distribution of noncorrelated oxygen vacancies leads to inconsistencies. On the other hand, we have to find a picture that reconciles the homogeneous characteristic of the normal transport properties[5,6,16] and the anomalous increase of the electrical resistance with extremely small changes of oxygen mass.

The picture we propose is consistent with that suggested[8,22] to explain the granular behavior in the superconducting state. In this case the material is considered to be made of homogeneous superconducting regions surrounded by a percolating insulating matrix, through which the quasiparticles and Cooper pairs can tunnel. As a consequence the thickness of the intergrain material is expected to be of the order of the coherence length ($\simeq$ 20 Å).

In what follows we discuss the application of this model to the conduction in the normal state, assuming that quasiparticles tunnel between metallic islands through the insulating material. Oxygen depletion is known[8,14] to decrease the critical current of the Josephson junctions between the superconducting regions. This is consistent with the results obtained in the normal state where oxygen depletion increases the tunneling resistance through the quasi-two-dimensional insulating barriers. This tunneling is an elastic scattering process that makes a contribution to τ_e in Eq. (2). This explains naturally the high correlation of the oxygen vacancies at the beginning of the evolution of the resistance toward its equilibrium value.

The small change in resistance with weight measured after the steep change in resistance, as shown in Fig. 3, is consistent with an electron scattering against a uniformly distributed concentration of vacancies, in the bulk of the grains. A calculation of σ_{eff} in this regime, using expression (4), gives $\sigma_{\text{eff}} = 3$ Å^2.

The hysteretic relation between resistivity and oxygen content, Fig. 3, indicates that oxygen can move more easily in the intergranular material, either leaving or penetrating the sample. This suggests that the percolating intergranular material contains a high density of oxygen vacancies which provide easy paths for oxygen diffusion.

The experimental results show that the normal transport properties can be treated as those of a homogeneous material with a single type of carrier, confirming previous results.[6,16] The material separating the metallic grains only contributes to the tunneling of quasiparticles, incorporated as part of their elastic scattering mechanism.

The oxygen depletion in the ceramic cannot be taken as distributed homogeneously in the bulk of the material. It becomes clear that part of the oxygen leaves or penetrates the material around the metallic grains while the rest changes the oxygen content of the intragranular material. This result invalidates most of the quantitative correlations made between the change of physical properties, as electrical conductivity or superconducting critical temperature, and the oxygen content. As an example, we estimate from the results of Fig. 3 that 30% of the total change in oxygen corresponds to that in the barriers.

The results discussed in this paper show the difficulties in assigning a meaningful value to the oxygen content of an x-ray homogeneous sample of the La-Sr-Cu-O system. This, together with the recently remarked[23,24] difficulties of understanding the local crystallographic structure as well as its composition, as a function of Sr content, shows that the understanding of the properties of one of the earliest and most simple high-temperature superconductors is far from being complete. The granular picture of these polycrystalline materials is shown to be useful to understand their transport properties in the normal state and justifies treating them within a homogeneous electronic picture.

As already explained, the intergranular material must necessarily have a particular topology around the superconducting metallic grains. This topology can be related to the formation process of the metallic grains [having a well-defined Sr content of ~ 0.16 (Refs. 24 and 25)] via an incipient spinodal-type decomposition occurring upon cooling from the fully homogeneous high-temperature solid solution. In fact, this decomposition is consistent with the approximate phase diagram for $La_{2-x}Sr_xCuO_4$ recently proposed by Jorgensen *et al.*[24] which shows the existence of a miscibility gap in the range $0.15 \leq x \leq 0.5$. Hence, we think that for $x = 0.2$ the observed granular behavior might correspond to coherently segregated regions of $La_{1.84}Sr_{0.16}CuO_{4-\delta}$ (the superconducting islands) and deformed $La_{1.5}Sr_{0.5}CuO_{4-\delta}$ (the intergranular material) which coexist throughout the sample conserving a common La_2CuO_4-type cationic frame.

The results also show that the study of superconducting properties in materials with very short coherence length provides a powerful tool to detect microscopic structural inhomogeneities at a scale much smaller than that studied by standard metallurgical methods.

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