Metallic to variable-range-hopping transition controlled by oxygen content in La-Sr-Cu-O

E. J. Osquiguil, L. Civale, R. Decca, and F. de la Cruz
Centro Atómico Bariloche and Instituto Balseiro, 8400 Bariloche, Río Negro, Argentina
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We have performed electrical resistivity measurements on the superconductor $La_{1.8}Sr_{0.2}CuO_{4-\delta}$ over a wide range of temperatures and oxygen concentration. The results provide experimental evidence for a transition from a metallic behavior at high temperatures to a variable-range hopping regime at low temperatures. The transition is controlled by the oxygen content. Correlation between both regimes is also shown.

The electrical resistivity of the high-critical-temperature superconductors[1,2] has an unusual[3-5] behavior. The high-temperature data show[3,4] no saturation, indicating an electron mean free path l which is long compared to interatomic distances. The resistivity[4,5] as well as the superconducting transition width[4] are extremely sensitive to oxygen content. Changes induced by heat treatments are reversible[4] with oxygen concentration. This result indicates that structural relaxation effects, if any, are of minor importance compared to the variation induced by oxygen absorption or desorption. The study of the resistivity as a function of temperature and oxygen heat treatments has led to the conclusion[4] that La-Sr-Cu-O ceramic superconductors should be considered as high-K materials in the clean limit. Metallic behavior is found in the $La_{1.8}Sr_{0.2}CuO_{4-\delta}$ system only in a narrow range of oxygen concentration. As soon as oxygen content is reduced in tenths of a percent the low-temperature resistivity changes from a behavior of the form[3,4]

$$\rho(T)=\rho(0)+\alpha T \quad (1)$$

to a "semiconductinglike" character. Oxygen losses up to 1% do not modify the onset of the superconducting transition T_{c0}, increase $\rho(T_{c0})$ by more than two orders of magnitude, or enlarge the transition width. Further reduction lowers T_{c0} and suppresses the superconducting percolation. These results were used to conclude[4] that oxygen vacancies induce the inhomogeneous superconducting character of the material, indicating that changes in the oxygen content modify the local electronic properties of the system. The correlation between these and the semiconductinglike behavior of $\rho(T)$ remains to be determined.

In this work, we focus our attention on the study of the possible interrelation between the low- and high-temperature regimes of $\rho(T)$. The sample preparation method and the experimental procedure were reported in Ref. 4.

Figures 1 and 2 show the resistivity of $La_{1.8}Sr_{0.2}CuO_{4-\delta}$ as a function of temperature. Data correspond to two different samples cut from the same ingot, after several heat treatments, consisting of vacuum annealings at 770 or 1045 K. Heat treatments at different temperatures change only the kinetics of oxygen desorption. The resistivity depends solely on the oxygen content.[4] Ther-

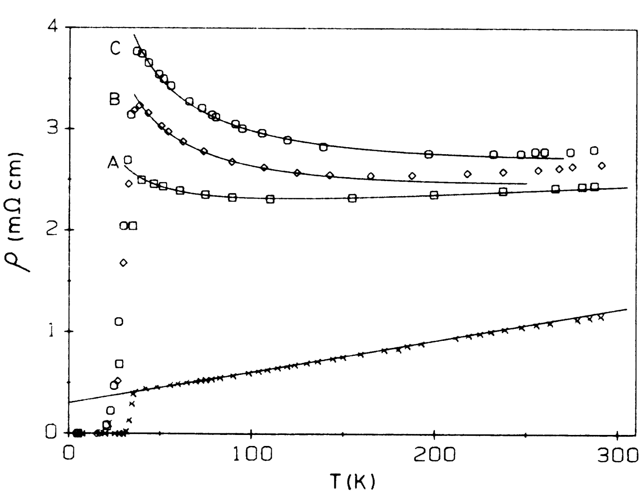

FIG. 1. Resistivity as a function of temperature for two samples of $La_{1.8}Sr_{0.2}CuO_{4-\delta}$ after several vacuum annealings at 770 or 1045 K. Curves A, B, and C (solid lines) are fits with variable-range hopping model. Fit parameters are listed in Table I. Lower curve corresponds to a sample in the metallic regime.

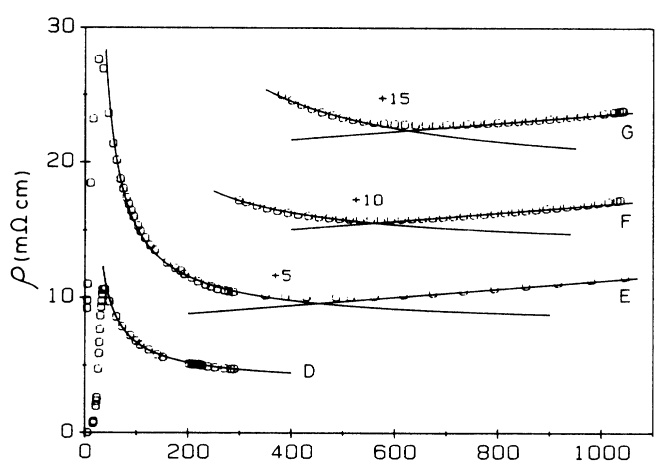

FIG. 2. As in Fig. 1, for the same samples after further reduction. For the sake of clarity curves E, F, and G have been offset by adding the constants indicated on each curve (in mΩ cm).

mogravimetric measurements[6] point out that the full resistivity range shown in the figures corresponds to a variation in oxygen content of about one percent. The experimental data in Figs. 1 and 2 indicate that at high enough temperatures, and for all heat treatments, $\rho(T)$ follows the linear temperature dependence given by (1). It is clearly seen that α does not depend on the oxygen concentration, even in samples where $\rho(0)$ has been increased by a factor of 20. From the experimental data it is found that $\alpha = 3.1\ \mu\Omega\,\text{cm/K}$ in agreement with other results.[7] This constancy of the value of α and its independence of the sample preparation method suggests that the linear temperature dependence in (1) represents an intrinsic transport mechanism characteristic of the ceramic superconductors. An identical conclusion was obtained by Tozer *et al.*[8] by measuring the resistivity of $YBa_2Cu_3O_{7-\delta}$ single crystals. Gurvitch and Fiory[3] argued that the change in α due to the variation of the density of states at the Fermi level, $N(0)$, induced by oxygen desorption, is canceled out by the phonon relaxation time dependence on $N(0)$. Although this explains the α independence on $N(0)$, it is not clear why α is sensitive to the change in Sr concentration.[9]

It is also seen from Figs. 1 and 2 that $\rho(0)$ increases when the sample is deoxidized and the transition from semiconductinglike to metallic behavior shifts to higher temperatures. This transition is characterized by a minimum in the resistivity, ρ_{min}. The correlation between the low-temperature regime and $\rho(0)$ becomes apparent if we plot ρ_{min} as a function of $\rho(0)$ (see Fig. 3). An interesting feature is the proportionality between ρ_{min} and $\rho(0)$, implying that the semiconducting character disappears only if the resistivity follows the ideal metallic behavior in the whole temperature range. This statement is valid within $\pm 50\ \mu\Omega\,\text{cm}$; the error has its origin in the definition of $\rho(0)$. It is convenient to point out that by ideal metallic limit we mean that $\rho(T)$ is linear at high enough temperatures, approaching zero at zero temperature, following some intrinsic dependence not experimentally accessible due to the superconducting transition. We have not been able to obtain this ideal metallic state by oxidizing the sample at 770 K in an oxygen atmosphere at normal pressure. As mentioned in Ref. 4, the resistivity decreases with oxygen absorption, reaching a saturation value shown by the lower curve in Fig. 1. Unfortunately, the thermogravimetric data are not precise enough to determine whether saturation implies that the crystal structure is unable to accept more oxygen under the experimental condition described before.

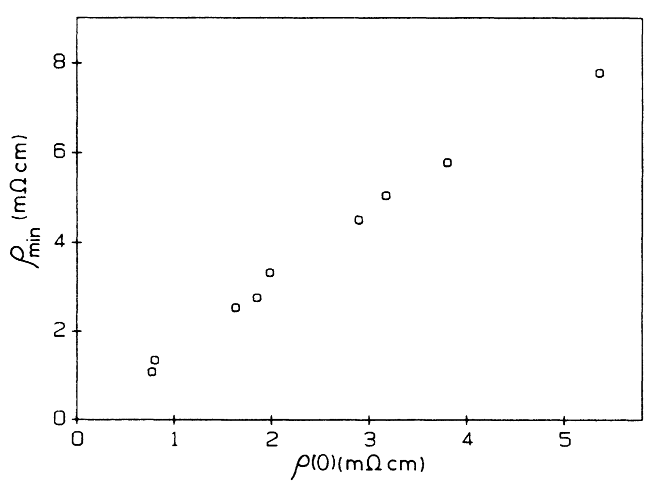

FIG. 3. Resistivity at the minimum as a function of $\rho(0)$, see text.

This suggests that $La_{1.8}Sr_{0.2}CuO_{4-\delta}$ has an optimum oxygen concentration where the conductivity should be that of an ideal metallic material. Therefore, the metallic character in the whole temperature range about T_{c0} can only be obtained in a very limited range of oxygen concentration. Due to the experimental error in the definition of $\rho(0)$, the hypothetical resistivity of a sample with the optimum oxygen stoichiometry could have a $\rho(0) < 50\ \mu\Omega\,\text{cm}$ that could take into account the elastic electron scattering with sample imperfections.

The change from metallic to semiconductinglike behavior due to changes in the oxygen content of a few parts of a percent points toward a peculiar behavior of the density of states at the Fermi level.[10] Within this context, the paper by Kastner *et al.*[11] is particularly relevant. They have measured the nonmetallic nonsuperconducting $La_{2-y}Sr_yCu_{1-x}Li_xO_{4-\delta}$ system and show that the resistivity in a wide range of temperatures follows the expression

$$\rho(T) = R\left(\frac{T}{T_0}\right)^{1/2} e^{(T_0/T)^{1/4}}, \tag{2}$$

characteristic of the variable range hopping mechanism[12] (VRH).

We have found that expression (2) also fits our data in the low-temperature regime, as shown in Figs. 1 and 2. Table I shows the parameters used to fit the data. For samples of similar room-temperature resistance, our parameters are in agreement with those obtained in Ref. 11. The linear fit corresponding to the high-temperature limit is also included. We see that expressions (1) and (2) provide an excellent description of the experimental results from 40 to 1000 K. It should be remarked that the theoretical fit is not accomplished by adding both expressions. It is the result of adjusting expression (1) in the high-temperature range and expression (2) in the low-temperature side. It might be argued that since the superconducting behavior is typical of inhomogeneous systems,

TABLE I. Fitting parameters for samples characterized by variable-range hopping conductivity shown in Figs. 1 and 2.

Curve	T_0 (K)	R (mΩ cm)
A	1880	1.260
B	4220	1.340
C	5100	1.470
D	20 300	2.190
E	61 500	1.750
F	73 000	2.150
G	171 000	2.080

the same criterion could be applied to the transport properties in the normal state. Nevertheless, the experimental results discussed in this work provide evidence indicating that the electrical transport in the ceramic is characteristic of homogeneous materials, in spite of its known intrinsic anisotropy and its inhomogeneous superconducting character. Preliminary magnetization results show that oxygen depletion strongly reduces the average superconducting order parameter in the bulk of the material. The fully oxygenated sample shows[13] a zero-field-cooling flux expulsion of 45%, at fields below the H_{c1} of the superconducting grains. After the sample is deoxygenated to obtain the resistivity indicated by curve A in Fig. 2, the field expulsion below H_{c1} is less than 20%. This result rules out the possibility that the oxygen loss takes place only from the same localized regions in the sample, i.e., at the grain boundaries.

It is reasonable to suggest[14] that the ceramic is a collection of grains of superconducting material surrounded by a semiconducting matrix. To take into account the experimental results, the proportion of semiconducting material as well as its resistivity should increase when decreasing the oxygen concentration. In this model, the low-temperature resistance will be dominated by the semiconducting matrix, while the metallic regions will dominate the resistance behavior at high temperatures. In this case, an expression obtained by adding (1) and (2) might be considered adequate. The fit of the experimental data is found to be as good as that shown in Figs. 1 and 2. Nevertheless, we believe this agreement is rather artificial: different curves are fitted changing not only the parameters R and T_0 (reasonable within the model) but also with different $\rho(0)$ and α. This result seems to be unphysical since, in order to reproduce the constant experimental slope of the metallic regime, every fitting curve is obtained using different α.

We have also tried to fit the data using a sample activated process instead of the VRH expression and the recently suggested[15] temperature dependence $\rho(T) = AT + B/T$. None of these expressions alone fit the experimental data. Again, a three-parameter fitting is acceptable but suffer from the same artificial behavior as discussed previously. We believe that this argument together with the fact that at low temperatures the data are adjusted with only two parameters show that the transport properties in the normal state are typical of homogeneous systems.

The ideas introduced in Ref. 11 can be applied to our results for samples with lower electrical resistivity. The effect of oxygen concentration would be essential in determining the degree of disorder, either in the metallic or localized regimes. The sensitivity to oxygen concentration would indicate[10] that the Fermi energy lays close to the mobility edge. As in Ref. 11, we have no evidence for simple activated conductivity and, surprisingly, we have a direct transition from the localized to the metallic state. The reason for this transition is not clear although it might be related to a temperature modification of the electron correlation effects.[10]

In summary, we have shown that the most relevant effect of the sample oxygen content on the electrical transport properties is to control the transition from the metallic to the localized regime. The theoretical fit of the low-temperature resistivity follows the VRH behavior as suggested by Kastner *et al.*[11] for samples of much higher resistivity.

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