Solid State Communications, Vol.65,No.6, pp.491-494, 1988.
Printed in Great Britain.

0038-1098/88 $3.00 + .00
Pergamon Journals Ltd.

$La_{1.80}Sr_{0.20}CuO_{4-\delta}$ A CLEAN LIMIT SUPERCONDUCTOR

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(Received 21st October 1987 by M. Cardona)

The electrical resistivity of the superconductor $La_{1.80}Sr_{0.20}CuO_{4-\delta}$ has been measured in a wide range of temperatures as a function of oxygen and vacuum heat treatments. The resistivity changes reversibly orders of magnitude with oxygen concentration. There is no sign of saturation at high temperatures, even for samples where the resistivity is increased by heat treatment in vacuum. Using the experimental data and general arguments it is concluded that the ceramic superconductors are high κ materials in the clean limit.

In this paper we present the measurements of the electrical resistivity, $\rho(T)$, of the high critical temperature superconductor[1] $La_{1.80}Sr_{0.20}CuO_{4-\delta}$, in a wide range of temperatures, as a function of oxygen heat treatment. The work was motivated by experimental results[2] indicating that the upper critical field Hc2(T) does not depend on the electrical resistivity of the material. This lack of correlation was found surprising since the high values of $\rho(300K) \simeq 2000\ \mu\Omega cm$ might suggest a superconducting behavior characteristic of the dirty limit[3]. Under the assumption that at high fields the flux penetration[4] is due to the increase of the vortex density, the upper critical field is reached when the core of the vortices overlaps. This argument does not imply a specific model of superconductivity and can be used to estimate the coherence length, $\xi(T)$. From the Hc2(T) measurements it is found [2,3,5] $\xi(0) \simeq 20Å$ for $La_{1.80}Sr_{0.2}CuO_{4-\delta}$ and $\xi(0) \simeq 7Å$-$30Å$ for $YBa_2Cu_3O_{7-\delta}$. These values are of the order of magnitude of the size of the crystallographic cell of the material and smaller than the coherence length of amorphous superconductors[6], where the electron mean free path, ℓ, is of the order of interatomic distances, a. Since the oxide superconductors are crystalline it is difficult to believe that ℓ is small enough to determine the effective coherence length. There are other results indicating that ℓ is larger than the interatomic distance: the low temperature "metallic" character of the resistivity, in contradiction with Mooij's criterium[7] and the lack of saturation in the resistivity at high temperatures. While writing this paper we received the preprints of the work done by Gurvitch and Fiory[8] and by Fiory et al[9] where attention has been focused on the last point made in the previous paragraph. From the analysis of the experimental data they conclude that ℓ is at least $6a$ at 1100 K. Considering the linear temperature dependence[8] of $\rho(T)$ the elastic mean free path turns out to be one order of magnitude larger. Therefore, it is reasonable to believe that the measured coherence length is characteristic of the superconducting material in the clean limit. The experimental verification of this suggestion is important for future comparison between experimental data and critical temperature calculations. Since the structure[10] of the oxide superconductors is anisotropic, it is reasonable to expect that the interaction responsible for superconductivity is also anisotropic. In the clean limit T_c is determined by the strongest electron coupling, while in the dirty limit the effective interaction results from an average over the Fermi surface lowering[11] T_c. Although we cannot give a definite answer to this question the investigation of the transport properties and its relation to superconductivity provides useful information to elucidate the problem.

In this work we show that $\rho(T)$ does not saturate at high temperatures, in agreement with ref.8. Heat treating the samples in vacuum increases the absolute value of the resistivity while maintaining the linear temperature dependence at high temperatures. Oxygen and vacuum heat treatment can be used to change reversibly the resistivity three orders of magnitude. It is shown that ρ does not correlate with the onset of the superconducting transition, Tco, but determines the superconducting transition width ΔTc. Samples with high resistivity do not show superconducting percolation and have a resistivity minimum

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below Tco. The inhomogeneous character of the material is made evident in the superconducting transition Although the microscopic origin of the inhomogeneity is not known it is likely present in the normal properties of the material, making the interpretation of the resistivity data difficult.

The sample in the shape of a rectangular bar of 0.04cm thick, 0.20cm wide and 1.2cm long was cut from an ingot of the ceramic material, prepared as described in ref.2. The density is 5.6g/cm^3 and was found X-ray single phase. The electrical measurements were made using the four probe method. The current and voltage leads were attached to the sample using silver paste and platinum lead wires[12]. A dewar was used to cover the range of temperature from 1 K to 300 K. Measurements at higher temperatures were made transfering the sample to a furnace where the gas atmosphere is controlled. The electrical resistivity data was taken point by point waiting for thermal equilibrium to be reached. The thermal relaxation time was always smaller than the typical time involved in oxygen desorption, except at temperatures very close to 1000 K. The data shown in this work are taken from a single sample but it was found reproducible in other samples cut from the same ingot.

The measurements reported in this paper are taken in conditions of non thermodynamic equilibrium. It is then necessary to know which is the time scale involved in the different processes that determine the physical phenomena under discussion. The results can be related to the change in the resistivity induced by a variation in oxygen concentration at constant temperature, or related to the temperature dependence of the resistivity at constant oxygen concentration. At high enough temperatures both effects might compete. Figure 1 shows the evolution of the resistivity at the highest temperature used in our experiments, T = 1045 K. The results are taken while pumping the experimental volume down to P = 10^{-5}mb. The results are fitted, full curve, by an expression of the form $\Delta\rho(t) = \Delta\rho(\infty)(1-e^{-t/\tau})$ where $\Delta\rho = \rho(t)-\rho(0)$, $\rho(0)$ = 4000 μΩcm, $\rho(\infty)$ = 16.000 μΩcm and τ = 470 minutes. $\rho(\infty)$ represents the equilibrium resistivity at 1045 K at the effective oxygen partial pressure where the experiment is performed. The oxygen desorption relaxation time is long compared to the time taken in a temperature run (typically half an hour) from 300 K to 1000 K. Within the experimental accuracy the evolution of the resistivity with heat treatment in vacuum is well represented by a single relaxation process. Structural neutron analysis[13] in powders of the same material show that the structure is stable under these heat treatments. Other important evidence of the structural stability is the reversible change in the resistivity when successive heat treatments in vacuum and oxygen are made. As shown later, the oxygen content determines uniquely the resistivity in the whole temperature range.

Figure 2 shows ρ as a function of temperature. The temperature dependence of the fully oxidized[14] sample is of the form $\rho(T) = \rho(0) + \alpha T$ up to the highest temperatures, with α = 3.4μΩcm/K. The resistivity is reversible with temperature up to 800 K. At 1000 K the rate of change of the resistivity due to oxygen desorption is noticeable in the time scale used in the temperature run. The variation of the resistivity at 1045 K shown in the figure is a consequence of maintaining the sample at that temperature during two hours. When cooling, ρ(T) has two regimes. At high temperatures ρ(T) decreases with the same α obtained when heating the sample fully oxidized. At lower

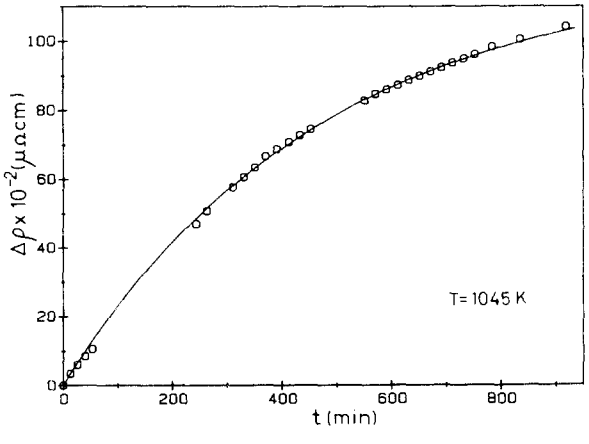

Figure 1: Time evolution of the resistivity in vacuum at T =1045 K. $\Delta\rho = \rho(t)-\rho(0)$, see text. Solid line represents $\Delta\rho(t) = \Delta\rho(\infty)(1-e^{-t/\tau})$, where τ = 470 min and $\Delta\rho(\infty)$ = 12000μΩcm.

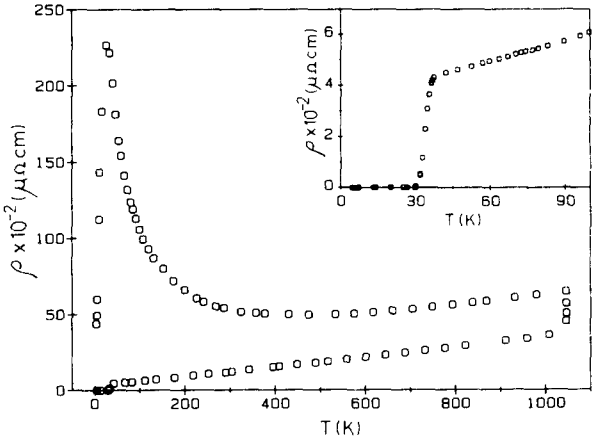

Figure 2: Temperature dependence of the resistivity. The lower curve corresponds to the fully oxidized sample. The vertical variation of ρ at 1045 K is a consequence of maintaining the sample at that temperature during two hours. Up to 800 K the curves are reversible in temperature in the time scale of an experimental run. The inset shows the superconducting transition for the fully oxidized sample.

temperatures the resistivity shows a semiconducting like behavior. The transition width increases so much that no superconducting percolation is found down to 4 K. These results clearly show that the effect of heat treatment cannot only be represented by a change in $\rho(0)$.

In Fig. 3 we plot the resistivity as a function of temperature in the low temperature regime, for different heating periods at 770 K. The successive runs and the conditions under which they were done are indicated in the figure caption. The results show that the heat treatment determines reversibly the behavior of the resistivity, proving that the change in resistivity is due only to processes related to the amount of oxygen in the sample. The behavior below Tco is interesting by itself and will be discussed elsewhere. The figure clearly shows the constancy of Tco and the change in ΔTc with the variation of the resistivity.

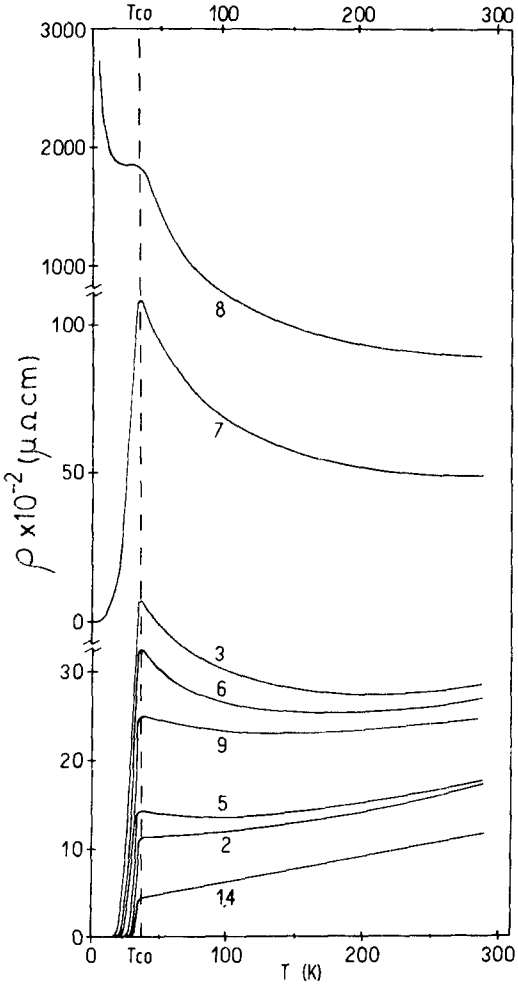

Figure 3: Temperature dependence of the resistivity in the low temperature regime for succesive heat treatments at 770 K. (1) fully oxidized sample. (2) 10h in vacuum. (3) 10h in vacuum. (4) 10h in 1 atm oxygen. (5) 37 h in vacuum. (6) 62 h in vacuum. (7) 30 h in vacuum. (8) 31 h in vacuum. (9) 20 min in 1 atm oxygen. The periods of heat treatment indicated for each run have to be added to the previous thermal history.

The data in Fig. 2 indicates that $\rho(T)$ does not saturate at high T after increasing $\rho(300\ K)$ by a factor of six when compared to the oxidized sample. If saturation is to be expected when $\ell \simeq a$ these results together with those of ref. 8 indicate that the electron mean free path is much longer than intera tomic distances. This argument supports our point of view that these superconductors should be treated in the clean limit. This conclusion is not surprising. Using an electron density[15] of $10^{21}\ cm^{-3}$ and an effective mass[16] of five times the electron mass we estimate the size of the electron pairs in the order of 20Å, in agreement with the values obtained from Hc2. This calculation follows from the rather general argument introduced by Pippard[17] based on the uncertainty principle. This small characteristic length turns out to be of the order of the distance between pairs. As a result of this unusual behavior it is possible to understand some experimental results typical of the ceramic superconductors. Superconductivity can be destroyed and recovered in distances of the order of the size of the primitive crystallographic cell. This explains why Tco is constant as far as some regions in the sample remain with the proper oxygen stoichiometry. This is a completly different behavior when compared to traditional superconductors where $\xi(0)$ is more than one order of magnitude larger. Within this picture it is clear that magnetic or other impurities will influence T_{co} only when the distance between impurities is of the order of $\xi(0)$. Measurements[18] of the superconducting transition in the $YBa_2Cu_3O_{7-\delta}$ as a function of Fe concentration replacing Cu, show that Tco starts to decrease when the average distance between Fe atoms is approximately $\xi(0)$. Following the same idea it is seen in Fig. 3 that Tco starts to decrease once the oxygen concentration is low enough (curve 8). Preliminary thermogravimetric data[19] indicate that the weight loss corresponding to that run is of the order of 0.2% of the total weight of the sample, about 1.2% of the oxygen content. This again corresponds to a density of vacancies with an average distance of the order of $\xi(0)$. We believe that the reduction of oxygen concentration changes the electronic properties of the material inducing a deterioration of its superconducting quality. Since the coherence length is small the deterioration is not shown by a homogenenous decrease of Tc but rather by a constant Tco and a large ΔTc. A question that remains without answer is how the local change of electronic properties influences the transport mechanism. We think that the answer lies in a better understanding of the transport properties and the meaning and value of the electron mean free path. Since in this materials $\ell > \xi(0)$ it is quite possible that the transport properties are better averaged on the sample than the superconducting ones.

In conclusion the measurements of the resistivity as a function of temperature and oxygen concentration show the extreme sensitivity of the normal and superconducting properties to the oxygen content. Using the experimental data and very general arguments we conclude that the ceramic superconductors can show the unique property of being a superconductor with a high Ginzburg-Landau parameter $\kappa \simeq 100$ remaining in the clean limit. If this suggestion is correct the electrodynamics of these materials should respond to a local clean limit behavior.

Acknowledgments - We thank C. Balseiro for useful discussions and A. López for a critical reading of the manuscript. This work was partially supported by the Consejo Nacional de Investigaciones Científicas y Técnicas of Argentina

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