Giant resistive peak close to the superconducting transition in $L_{2-x}Ce_xCuO_4$ single crystals

M. A. Crusellas, J. Fontcuberta, and S. Piñol
Institut de Ciència de Materials de Barcelona, Consell Superior de Investigacions Científiques, Campus Universitat Autònoma de Barcelona, Bellaterra, 08193, Spain
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We have measured the magnetoresistivity of some $L_{2-x}Ce_xCuO_{4-y}$ (L =Pr,Nd,Sm) superconducting single crystals along the *ab* plane and the *c* axis. For most crystals the resistivity along both directions displays a very sharp rise just below T_c and before the zero-resistance state is reached. This resistance anomaly is quenched by a magnetic field. The effect of the field is more pronounced for $H \| c$ than for $H \| (ab)$. Several possible scenarios to account for the resistance anomaly are discussed. We propose that the resistance peak is a manifestation of a quasireentrant behavior resulting from an intrinsic granularity of these *n*-type high-temperature superconductors. The relevance of these results and ac susceptibility measurements for the anomalous behavior reported for the upper critical field is discussed.

INTRODUCTION

Investigations of the temperature-dependent electrical resistivity in granular metals are of considerable interest because of their relevance to the problem of electron localization and the occurrence of superconductivity.[1] This interest has been renewed because high-temperature superconductors (HTSC) display in some aspects typical features of disordered superconductors. Granularity has been observed in HTSC single crystals[2,3] and it has been argued that intrinsic granularity can be at the origin of the controversy between Lorentz-force versus non-Lorentz-force-based dissipation mechanisms in some HTSC materials.[4]

In granular systems, single particle tunneling across the resistive barriers between superconducting islands[5] and charging effects[6] below T_c are expected to give rise to an increase of the resistivity above its extrapolated normal-state value. Josephson coupling between grains, on the other hand, has the opposite effect: pair tunneling between grains reduces the overall resistivity below T_c.

Competition of all these effects leads to the possibility[7] of a reentrant (or quasireentrant) behavior, which has been identified in a number of granular or very thin film superconducting systems.[8–10] Quasireentrance is manifested typically by a lowering of the resistance when the temperature is reduced below T_c, followed by a rapid increase at lower temperatures. Gerber *et al.*[11] have recently observed a double-peak superconducting transition in granular $L_{2-x}M_xCuO_{4-y}$ (L =Pr,Nd,Sm,Eu; M =Ce,Th) electronic superconductors, which has been explained in terms of a quasireentrant-like behavior associated with the polycrystalline nature of the samples.

On the other hand, in the electronic HTSC superconductors of the $L_{2-x}M_xCuO_{4-y}$ family, the upper critical field line in the H-T phase diagram appears to be quite puzzling for a number of reasons. For instance, close to T_c, $H_{c2}(T)$ determined from magnetization measurements shows an upward curvature that cannot be explained within the conventional Ginzburg-Landau theory.[12] In addition, $H_{c2}(T)$ shows a similar shape to the irreversibility line determined from both ac susceptibility experiments[13] and magnetization measurements.[14,12] One might speculate that these results, obtained from measurements performed on single crystals, originate from defects which may lead to some granularity-related effects. In fact, indications that even $L_{2-x}M_xCuO_{4-y}$ single crystals can be very defective, can be found in the large residual resistivity and the very small slope of $\rho(T)$ at a relatively high temperature (< 100 K).[15]

In this paper we report measurements of resistivity on $L_{2-x}Ce_xCuO_{4-y}$ single crystals (L =Nd,Pr). Particular attention has been devoted to the shape of the resistivity versus temperature curve close to the superconducting transition and its dependence on the crystal quality. The most striking result is the observation of a giant resistivity enhancement close to T_c. We find that slightly below T_c and in zero magnetic field, the resistivity of the crystal rises abruptly, reaching a maximum value $\rho(T_p)$ at a temperature $T_p < T_c$. At lower temperatures a sharp drop of resistance signals the onset of the overall superconductive state. It is important to notice that similar absolute values of the excess resistivity $\Delta\rho = \rho(T_p) - \rho(T_c)$ are obtained for both the in-plane resistivity $[\rho_{ab}(T)]$ and the *c*-axis resistivity $[\rho_c(T)]$. Here, $\rho(T_c)$ is the resistivity at T_c. The amplitude of the peak $\Delta\rho$ is lowered by the application of a magnetic field. The effect is more pronounced for $H \| c$ than for $H \| (ab)$. Increasing the measuring current has an effect on the peak amplitude similar to the application of a magnetic field.

We will discuss the origin of this anomalous resistivity peak by arguing that it is a clear manifestation of an intrinsic granularity which appears to be a common signature of most *n*-type HTSC single crystals. We will show that the amplitude of the resistive peak can be modified by an appropriate thermal treatment of the crystal and thus may not exist in ideally perfect single crystals. However, we will argue that because of the inherent defective character of the CuO planes in the Ce and oxygen vacancy doped materials, electromagnetic and transport properties reflecting this inhomogeneous character could be generally expected.

EXPERIMENTAL

Single crystals of $L_{2-x}Ce_xCuO_{4-y}$ (L = Pr,Nd) were grown by the self-flux method.[16] To induce superconductivity, the samples were reduced under Ar in two steps: first, at 900 °C for 12 h and second at 600 °C for 15 h. To measure the resistivity, four strips of Au paint were prepared and cured at 400 °C for 15 min under Ar. Pt wires (50 μm) were attached to the contacts by using silver paste. The contact resistance was smaller than 2 Ω. Two different contact configurations have been used: (a) four parallel strips (A,B,C,D) on each face of the crystal and (b) four small dots at the corners of the crystal. Figure 1 shows a schematic drawing of the contact arrangements.

We will present and discuss here the data obtained on crystals of $Nd_{1.85}Ce_{0.15}CuO_{4-y}$ ($2.2\times3.2\times0.2$ mm^3) and $Pr_{1.85}Ce_{0.15}CuO_{4-y}$ ($2.1\times1.1\times0.5$ mm^3) measured by using the parallel strip contact configuration. However, the existence of the resistivity peak[17] and its dependence on H and the testing current have been observed to be independent of the contact configuration. Most of the measured crystals, but not all, display the resistivity anomaly. It will be argued below that the anomalous peak is related to some intrinsic granularity of the single crystals. However, no clear correlation has been found between the room-temperature resistivity and the observation of the resistance peak. It may be that at temperatures far from T_c, the resistance is less sensitive to small gradients or discontinuity of concentration of Ce or oxygen.

The data reported here were obtained with both the current (I) within the ab plane and along the c axis. In this latter case the current was symmetrically fed through the (A,D) contacts [Fig. 1(a)] and drained through the equivalent contacts on the bottom of the crystal. The potential was measured between the contact B and its equivalent on the bottom. Both ac (16 and 80 Hz) and dc current biases were used with identical results. The magnetic field was oriented either parallel to the c axis or perpendicular to it. I and H were always perpendicular.

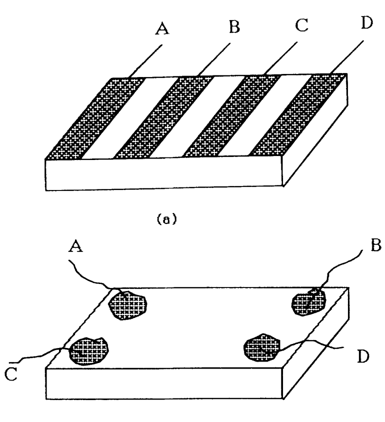

FIG. 1. Contact configurations used to perform electrical resistivity measurements. c-axis resistivity was measured only by using the arrangement (a) with contacts strips (not shown in the figure) on each side of the crystal.

RESULTS AND DISCUSSION

Figure 2 shows the temperature dependence of $\rho_{ab}(T)$ and $\rho_c(T)$ for the $Nd_{1.85}Ce_{0.15}CuO_{4-y}$ single crystal. Two remarks are in order. First, at $T > 30$ K both resistivities have a metallic character. Second, an anomalous enhancement of resistance is observed in both $\rho_{ab}(T)$ and $\rho_c(T)$ at temperatures close to the superconducting transition. A similar behavior is observed for the measured $Pr_{1.85}Ce_{0.15}CuO_{4-y}$ crystal. Due to the fact that $\rho_c(T) \gg \rho_{ab}(T)$ and the metallic character of $\rho_c(T)$, the observation of the resistive peak in $\rho_c(T)$ is important because it strongly indicates that this anomaly is not caused by the mixing of $\rho_{ab}(T)$ and $\rho_c(T)$ components in the measured resistivity.

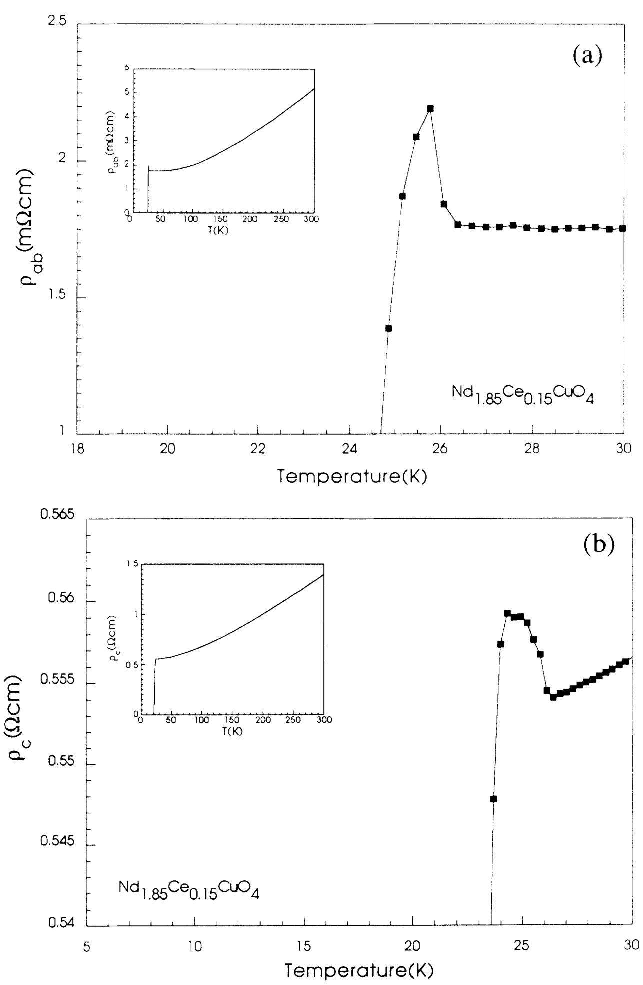

FIG. 2. In-plane (ρ_{ab}) and c-axis (ρ_c) resistivity as a function of temperature for a $Nd_{1.85}Ce_{0.15}CuO_4$ single crystal.

It is well known that the contact geometry used to perform the measurements of the in-plane resistance cannot give accurate values of ρ_{ab} in anisotropic systems because of the inhomogeneous current feeding and draining. As a result, some mixing of ρ_{ab} and ρ_c is expected to occur at any temperature. However, any current redistribution cannot enhance both ρ_{ab} and ρ_c simultaneously, just close to the superconducting temperature. Consequently, the resistivity anomaly reflects an inherent property of the measured inhomogeneous crystals and it is not an experimental artifact caused by any current redistribution.

Figure 3 shows the potential drop across the voltage leads (B,C) when the current (400 μA) is injected through the contacts (A,D). A striking resistive peak is apparent close to T_c. Figure 3 also shows the potential drop across (A,B) when current is injected through (C,D). A similar result is obtained when the current leads are changed to (A,B) and the potential is measured by (C,D). The onset of superconductivity (T_c) is very sharp and takes place just at the temperature where the anomalous peak starts to develop. Therefore, the excess resistance develops well below T_c and thus the peak occurs at $T_p < T_c$. The observation of a nonzero voltage drop between contacts C and D, when current is fed through (A,B), suggests that the crystal has some inhomogeneous character. Any other contact configuration always makes observable the resistance peak. As shown in Fig. 4, increasing I leads to a slight reduction of $\Delta\rho(T_p)$, but the onset of the anomaly remains at the same temperature.

The effect of an external magnetic field on the in-plane resistivity amplitude $\Delta\rho$ for the $Pr_{1.85}Ce_{0.15}CuO_{4-y}$ crystal is shown in Fig. 5. For this particular crystal and for $H \| c$, the resistance anomaly vanishes for $H = 1$ T. As mentioned above, for $H \| c$ the suppression of $\Delta\rho$ is much faster than for $H \| (a,b)$. In Fig. 6 we show the magnetic field effect on the c-axis resistivity amplitude $\Delta\rho$ for the $Nd_{1.85}Ce_{0.15}CuO_{4-y}$ single crystal. Notice that neither $\rho_c(T)$ nor $\rho_{ab}(T)$ changes abruptly close to $T_c(H=0)$ when the peak is suppressed by the field; consequently,

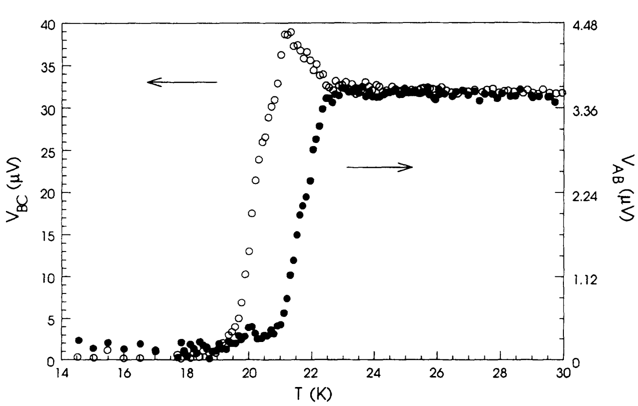

FIG. 3. Open symbols: Potential drop across (B,C) contacts when the current is injected through (A,D). Solid symbols: Potential drop across (A,B) when current is injected through (C,D) for a $Pr_{1.85}Ce_{0.15}CuO_4$ single crystal.

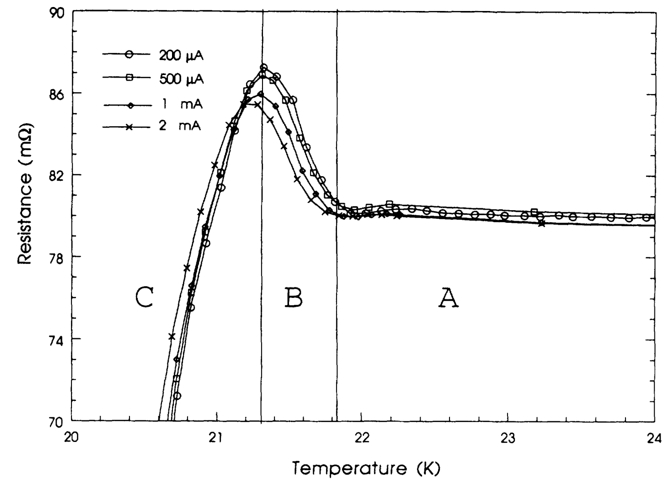

FIG. 4. Effect of the measuring current on the amplitude of the resistance peak $\Delta\rho$ of the $Pr_{1.85}Ce_{0.15}CuO_4$ single crystal: $I = 200$ μA (○), 500 μA (□), 1 mA (◇), and 2 mA (×). Note that only the upper part of the resistive transition is shown. The A, B, and C regions are discussed in the text.

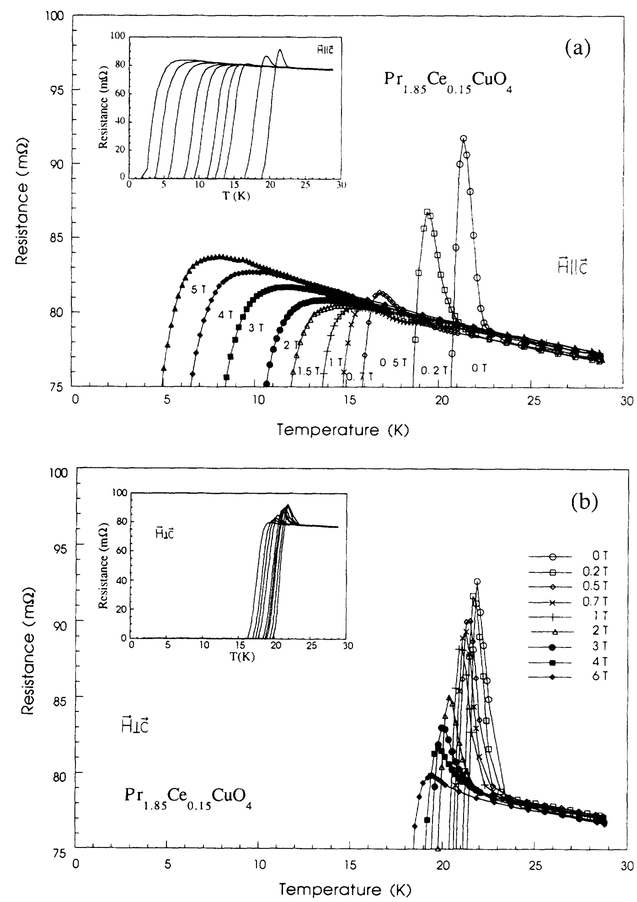

FIG. 5. Effect of an external magnetic field on the amplitude $\Delta\rho$ of the in-plane resistance peak for the $Pr_{1.85}Ce_{0.15}CuO_4$ single crystal. (a) $H \| c$ and (b) $H \| (a,b)$. Notice that the y-axis scales are enlarged to clearly reveal the effect of the field. The insets show the full resistive transition.

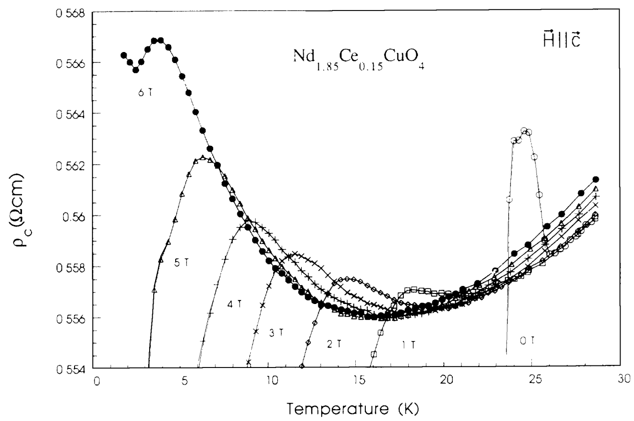

FIG. 6. Effect of an external magnetic field ($H \| c$) on the amplitude $\Delta\rho$ of the c-axis resistance peak for the $Nd_{1.85}Ce_{0.15}CuO_4$ single crystal. Only the upper part of the transition is shown.

the resistivity anomaly is not related to the normal-state temperature dependences of ρ_{ab} and ρ_c.

This nonmonotonic magnetic field and current-dependent behavior of the resistance is surprising, especially in view of the monotonic variation of $\rho_{ab}(T)$ and $\rho_c(T)$, which is found when the peak is suppressed by the field (see Figs. 5 and 6). We have observed this behavior in many $L_{2-x}Ce_xCuO_{4-y}$ single crystals and different contact configurations.

Reports on the existence of anomalous resistivity peaks close to T_c can be found for a variety of superconducting systems. The significance of some of the proposed mechanisms in the present situation can be readily excluded.

Recently, Briceño *et al.*[18] have reported that in $Bi_2Sr_2CaCu_2O_8$ single crystals, when current and field are both parallel to the c axis, a resistance maximum occurs, even in zero field, due to competition between semiconducting $\rho_c(T)$ and Josephson interplanar coupling. The effect of an external field ($H \| c$) was to extend the normal-state (semiconductor-like) behavior towards lower temperatures and thus to higher values of resistivity before the sharp drop of resistivity to zero occurs. In our case, as data of Fig. 6 clearly show, the magnetic field also extends the normal state to lower temperatures. What is more important, and distinct, is that the peak rises the resistivity *above* the extrapolated $\rho_c(T)$ normal-state resistivity. Therefore an explanation similar to that suggested by Briceño *et al.*[18] is ruled out.

Gordon *et al.*[19] have found by magnetoresistance measurements on Al films that the inelastic electron scattering rate increases when T approaches T_c from above, because of an interaction between superconducting fluctuations and conduction electrons. The fluctuations are weakened by a small magnetic field and thus a reduction of the resistance anomaly has been observed.[20] In disordered Cu-Zr alloys the existence of dilute magnetic impurities also leads to a strong increase of scattering of conduction electrons in a narrow temperature range above T_c.[21] Pictures based on interactions between superconducting fluctuations and charge carriers or spins can be ruled out by the results shown in Fig. 3: when the current is injected and drained through two adjacent contacts, the resistive transition is very sharp and occurs at $T_c = 22.5$ K, well above the maximum in $\rho(T_p)$. Therefore, if we assume that all superconducting parts of the crystal have the same critical temperature T_c, we should conclude that the peak develops below the onset of superconductivity and it does not appear to be related to fluctuations. The picture based on the enhanced electron scattering by superconducting fluctuations could not be ruled out if $T_c \approx 22.5$ represents only the critical temperature of a particular region of the crystal.

Kwong *et al.*[22] have reported the observation of an enhancement of the resistivity above the normal-state value in an Al thin film containing regions of different transition temperatures. The peak occurs slightly above the transition temperature of the lower-T_c section. It has been argued that the observed anomaly could be understood as arising from the mismatch of the quasiparticle and Cooper pair potentials at the interface between N-S regions. To observe this effect, the voltage probes should be placed within a distance of the quasiparticle potential decay length, which is, of course, much shorter than the contact separation. Our observation of the resistivity anomaly for different contact configurations rules out this interpretation.

To account for our experimental data, we propose here a new model that includes explicitly the intrinsic granularity of n-type single crystals. We will assume that regions of distinct T_c and/or superconducting islands surrounded by nonsuperconducting material can exist within the crystal. The existence of these inhomogeneities is very plausible because of the strong dependence of T_c on the oxygen contents of the sample. Variations on the oxygen content of 0.04 at/f.u. produce the quenching of the superconductivity in $L_{2-x}Ce_xCuO_{4-y}$.[23] In addition, the reduction process has an optimal time to get the maximum T_c, otherwise shorter or longer reductions lead to a deterioration of T_c.[24] Both considerations prompt us to assume that reduced single crystals of large size can be intrinsically inhomogeneous. Indeed, a recent single-crystal x-ray work has shown that in the particular sample studied, regions with different c-axis lattice parameters coexist.[25] With this assumption, the crystals can be viewed as a granular system and the peak anomaly would be a manifestation of a quasireentrant behavior similar to that observed by Gerber *et al.*[11] Notice in Fig. 2(c) of Ref. 11(b) an appreciable enhancement of the resistance above its extrapolated normal-state value.

In Fig. 4 we have indicated different regions where distinct transport mechanisms dominate $\rho(T)$. In region A the material is an ohmic metal with a positive resistivity slope and dV/dI constant, as is shown in Fig. 7. At $T_c \approx 22.5$ K, the superconductive islands and/or the regions of higher T_c (denoted SC) become superconducting. Below this temperature, in region B, the transport of charge between SC zones can take place via thermally activated single electron hops with an activation energy being determined by the superconducting gap and the charging energy.[5] Since the number of quasiparticles de-

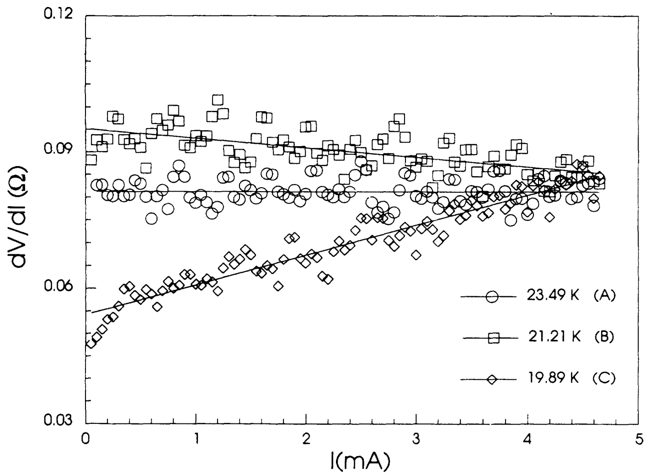

FIG. 7. Slope of the V-I characteristics for the $Pr_{1.85}Ce_{0.15}CuO_4$ single crystal measured at temperatures in the A, B, and C regions of the $R(T)$ curve of Fig. 3.

creases as the temperature is lowered and because of their ability to overcome any charging energy barrier decreases, the resistivity should increase below T_c. In this region, the material is expected to show some non-ohmic behavior.[5] Indeed, as shown in Fig. 7, the I-V characteristics below T_c are no longer linear. Their slopes slightly decrease when I increases. In contrast, in region C, the slope of dV/dI is positive. Cooper pair tunneling sets in when two neighboring SC regions become Josephson coupled. In the absence of a charging energy, this condition is that the Josephson-coupling energy $E_J(T)$ exceeds the thermal energy, i.e., $E_J(T) \approx (\hbar/e^2)\Delta(T)/R_n > kT$, where $\Delta(T)$ is the gap in each SC island and R_n is the normal-state resistance of the junction. At a certain temperature $T < T_p$, the condition $E_J(T) > kT$ is fulfilled and Cooper pair tunneling leads to a reduction of the resistivity (region C). This simple model accounts qualitatively for the observed $\rho(T)$ behavior. Quantitative analysis would require a detailed knowledge of the size and critical temperature of the SC regions as well as the resistance and thickness of the junctions between them which, at present, are largely unknown.

We now consider the observed dependence of the resistance anomaly on magnetic field. Following the argument given above, the amplitude $\Delta\rho$ of the peak is related to the order parameter within each SC region. Therefore, the presence of a magnetic field will reduce $\Delta\rho$ if the reduction of the order parameter by the magnetic field overcomes its enhancement caused by the shift of the peak to lower temperatures. Under such assumptions, in agreement with our experimental data, the resistance anomaly will be quenched by the magnetic field.

The origin of the remarkable anisotropy of the magnetic field effect on the resistance peak is not yet very clear. However, it is conceivable that it can result from the intrinsic granularity of the crystal, which is expected to be more pronounced within the ab plane than along the c axis. Alternatively, the strong anisotropy of the effect of the magnetic field on the amplitude of the peak may result from the anisotropy of the upper critical fields in these materials (see insets in Fig. 5). The shift towards lower temperatures of the resistivity curves is very different for $H\|ab$ than for $H\|c$, thus resulting in a distinct contribution of quasiparticles and pair tunneling.

The assumption of the existence of granular effects in these single crystals can be tested by further annealing the crystal. It is expected that low-temperature annealing will not change the overall oxygen content but will only induce some reordering of oxygen ions and consequently a modification of the internal granular structure of the crystal. Thus, we have annealed the crystal under Ar atmosphere at 400 °C for 8 h. The electrical contacts were not removed. Notice that the annealing is done under the same conditions that were used to cure the electrical contacts. In Fig. 8 we show the electrical resistivity versus temperature curve obtained after the low-temperature annealing process. Notice that the data of Figs. 3 and 8 were obtained by using a close-cycle He cryostat which is inherently noisier than the He bath cryostat used to perform the rest of the experiments. The low-temperature normal-state resistivity changes slightly, but what is more important, the shape of the anomalous resistance peak has been strongly modified and $\Delta\rho(T_p)$ reduced. The zero-resistance temperature is also lowered.

These observations are important for two reasons. First, they provide additional evidence that the resistivity anomaly is not related to ρ_c and ρ_{ab} mixing because of the anisotropic electrical properties of the crystal. Second, these results clearly stress that the anomalous resistivity peak is strongly influenced by the defect distribution, which rules out any question about measuring artifacts and gives new support to our analysis of the results based on the existence of intergranular-like effects in these crystals. The shape of $R(T)$ in Fig. 8 clearly displays the characteristic features observed in reentrant systems.[10] It is also similar to the data reported by Gerber *et al.*[11] from their study of polycrystalline materials.

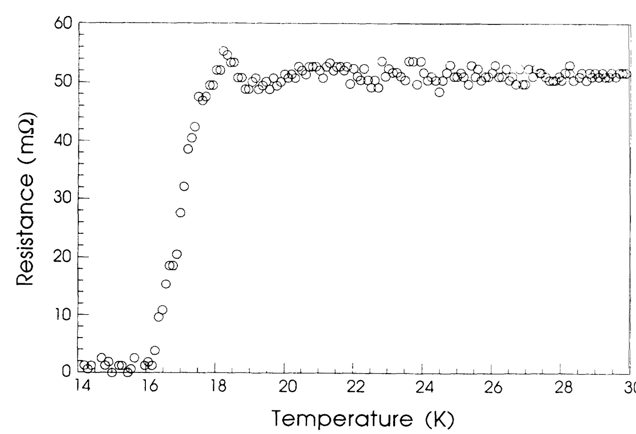

FIG. 8. Resistance vs temperature curve obtained after low-temperature annealing of the $Pr_{1.85}Ce_{0.15}CuO_4$ single crystal.

The role or influence that intrinsic granular effects can have on the reported upper critical fields $H_{c2}(T)$ and irreversibility fields $H^*(T)$ is far from being clear. However, it can be suggested that the observed weak dependence of the in-phase component of the ac susceptibility data[13] on the ripple field amplitude and the upwards curvature of $H_{c2}(T)$ (Refs. 12 and 14) are also different manifestations of defective crystals. It is clear that in all electron-doped copper oxides [the T' cuprates ($L_{2-x}Ce_xCuO_{4-y}$), or in the infinite layer $Sr_{1-x}L_xCuO_2$ (L =Nd,Pr,La)],[26] there is a delicate equilibrium between superconductivity and semiconductor-like, or charge-carrier localization behavior. Very precise synthesis conditions are required to prepare materials with optimal superconducting properties. Even in that case, the normal-state resistivity shows impurity dominated behavior close to T_c (Ref. 17) and a tendency towards localization at lower temperature when superconductivity is suppressed by a magnetic field. The transition widths are usually broad, and small Meissner fractions are a rule.[26] These experimental results, which are not commonly found in the other p-type superconducting cuprates, reflect the major importance of defects on the transport and magnetic properties of the electronic superconductors. It is worth noting that in $L_{2-x}Ce_xCuO_{4-y}$ of the T' structure, oxygen vacancies are mainly created within the superconducting CuO plane, whereas in most of p-type materials, hole doping is reached by changing the oxygen contents of the "charge reservoir," i.e., Cu-O chains along the b axis in 1:2:3 and 1:2:4, BiO layers in BiSCCO, ... Therefore, it may be suggested that this different location is the basis of the more pronounced dependence of the normal state and superconducting properties on the defect distribution in the electronic superconductors than in the hole-type superconductors. Nevertheless, we have also shown that an appropriate thermal treatment can reduce the relevance of the intrinsic defects (Ce substitution and oxygen vacancy distribution).

Summarizing, we have found in $L_{2-x}Ce_xCuO_{4-y}$ single crystals a giant enhancement of the resistivity just below the onset of the superconductivity. The resistivity both along the c axis and in the ab plane rises strongly before the zero-resistance state is reached. This anomalous resistivity peak is quenched by a magnetic field. We have proposed that the resistivity peak is a signature of a quasireentrant behavior that stems from the granular character inherent in most of these n-type HTSC single crystals.

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