Transport properties of $NdBa_2Cu_3O_{6+x}$ ceramics at the edge of the superconducting region upon a decrease in carrier density as a result of oxygen disordering in the $Cu–O_x$ planes

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An initially nonsuperconducting ceramic sample with the composition $NdBa_2Cu_3O_{6+x}$ is brought, by means of pressure and quenching, to a state with a high carrier density and a superconducting transition, after which it is returned to the initial state by gradual annealing in several steps. The evolution of the magnetoresistance of the sample showed that even in the most resistive state realized in the experiment the superconducting interaction influences the resistance of the sample at fields all the way up to 5–6 T. In an 8 T field the change in resistance in this state in the temperature interval from 0.4 K to 20 K is described well by a logarithmic law $\Delta R \propto \log T$. © *1997 American Institute of Physics.* [S0021-3640(97)00806-2]

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The transport and superconducting properties of the compounds $RBa_2Cu_3O_{6+x}$ (R is a rare-earth element) are determined by the hole density n_h in the CuO_2 planes. Holes arise because electrons are transferred from these planes to the $Cu–O_x$ chain planes. Studies by many investigators have established that n_h depends not only on the oxygen concentration x in the $Cu–O_x$ planes but also on the arrangement of the oxygen in these planes, which can vary on account of the finite mobility of the oxygen atoms even at room temperature $T_r \approx 300$ K. The variants of the oxygen arrangement reduce to distributing oxygen over $Cu_{y+1}O_y$ chains of different length y.

It is well known that the density n_h and the superconducting transition temperature T_c decrease when the samples are heated to $T > T_r$ and then quenched in liquid nitrogen.[1,2] As the temperature increases, long $Cu_{y+1}O_y$ chains break up into shorter fragments, and the fraction of fragments with $y \leqslant 4$, which do practically no trapping of electrons from the CuO_2 planes and do not contribute to the formation of the carrier density n_h in them, increases.[3,4] When the quenched sample is held at room temperature T_r, the chains gradually increase in length, so that their average length $\overline{y}$ assumes an

equilibrium value $\overline{y(x,T_r)}$ within approximately one day. Accordingly, the density n_h also returns to its equilibrium value.

It is also possible to act on the oxygen subsystem by means of an external pressure P (see Ref. 5 and the references cited therein). The decrease in the volume of the unit cell in the compressed sample results in a higher equilibrium value $\overline{y(x,T,P)}$. Quenching can also preserve such a state of high density n_h after the pressure is removed. Annealing of such a sample at room temperature will decrease n_h and, correspondingly, T_c.

At values of x for which the sample is at the edge of the superconducting region (with densities n_h close to the critical values), a larger interval of n_h values can be spanned by applying pressure than by increasing the temperature. In Ref. 6 a transition temperature $T_c \approx 30$ K was achieved in an initially nonsuperconducting ceramic sample $NdBa_2Cu_3O_{6.67}$ by applying pressure, and then, with the pressure removed, the sample was returned to the initial state by holding at room temperature. We employed the effect of Ref. 6 to track the evolution of the temperature dependence of the resistance and magnetoresistance near the edge of the existence region of superconductivity in a single sample, i.e., on a fixed structural background.

We obtained the ceramic $NdBa_2Cu_3O_{6+x}$ by solid-phase synthesis of a mixture of neodymium and copper oxides and barium nitrate at temperatures of 900–1000 °C for a time of 8 h in an oxygen flow, grinding the intermediate product once. From the powder obtained, samples in the form of tablets 10 mm in diameter and 1.3 mm thick were pressed at a pressure of 0.7 GPa. Sintering was performed in an oxygen stream at $T=1000$ °C for 15 h, followed by cooling to 425 °C at a rate of 1 deg/min and holding periods of 3, 15, and 20 h at 650, 580, and 425 °C, respectively. The oxygen index x in the samples was determined by iodometric titration to be equal to 0.94. It was decreased nearly to the critical value by heating the samples in a nitrogen stream at 458 °C for 20 h and then cooling to room temperature (the value of x was calculated according to the change in weight). The critical value of x in the neodymium ceramic (R = Nd) is much higher than in the yttrium ceramic (R = Y).[7,8] In our sample the index x was equal to 0.67, just as in Ref. 6.

The dimensions of the sample were approximately $1\times2\times5$ mm. The resistance was measured by the standard four-contact method with the aid of pressure contacts consisting of pointed gold wires. The measurements were performed in a cryostat with pumping on He-3 vapor; a magnetic field of up to 8 T was produced with a superconducting solenoid.

The initial state of the ceramic, equilibrium at room temperature, was characterized by a rapid growth of the resistance with decreasing temperature, without any indications of a superconducting transition (Fig. 1, curve #1). Next, the sample was subjected to compression to a pressure of 1.5 GPa at room temperature for 24 h. The pressure treatment was conducted in a piston–cylinder type apparatus. Silicone was used as the pressure transmitting medium. To prevent the silicone from entering the pores in the ceramic, the sample was placed inside a rubber sheath which transmitted hydrostatic pressure well. The chamber was disassembled at room temperature, the process requiring 8 min, after which the sample was quenched in liquid nitrogen. The placement of the sample in the holder with the contacts was done at liquid nitrogen temperature without heating the

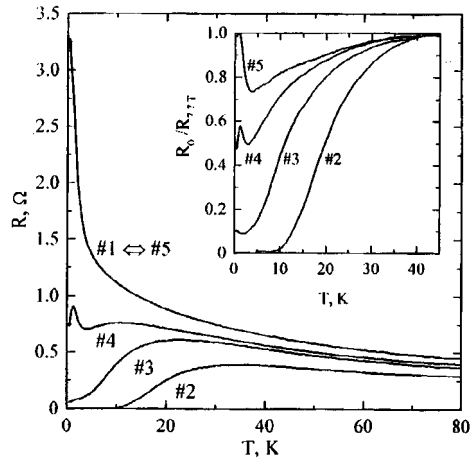

FIG. 1. Temperature dependences of the resistance of a $NdBa_2Cu_3O_{6.67}$ sample in zero magnetic field in states #1–#5 (states #1 and #5 are equivalent). Inset: Temperature dependences of the ratio of the resistances for all of these states in zero field and in a 7.7 T field.

sample. As a result, a sample with a complete superconducting transition starting at about 40 K and ending at 10 K was obtained (Fig. 1, curve #2). Next, the carrier density in the sample was decreased by heating the sample to room temperature; allowing the sample to stand for about 1 h substantially changed its state. In this manner, a series of different states was obtained (Fig. 1, curves #3 and #4). At the last stage the sample was held at room temperature for about two days. This gave the state #5, which, according to measurements of $R(T)$ and $R(H)$, was identical to the initial state, confirming that all changes are reversible.

In this manner, we obtained four states #2–#5 with different values of n_h and fundamentally different dependences $R(T)$. The magnetoresistance and its variation with temperature were measured for each state. The results are presented in the inset in Fig. 1 and in Figs. 2 and 3. We shall now proceed to a generalization and discussion of the results.

The superconducting response in granular materials has three components:[9]

a) London component — individual granules, becoming superconducting, shunt the resistance around themselves; this component is destroyed by the critical field $H_{c2}(T)$, which results in a positive derivative $\partial R/\partial H$;

b) Josephson component — a nondissipative current flows between neighboring superconducting granules and produces extended sections with no resistance; this state is destroyed by a field $H_J \ll H_{c2}$; and,

c) incoherent component — a single-particle current, which is less than the normal current because of the superconducting gap at the Fermi level, flows between a superconducting and a normal granule or between two superconducting granules but with the Josephson current suppressed; a field H, by destroying the gap, intensifies the single-particle current, which results in a negative derivative $\partial R/\partial H$.

These components all produce quite substantial changes in the resistance. For this

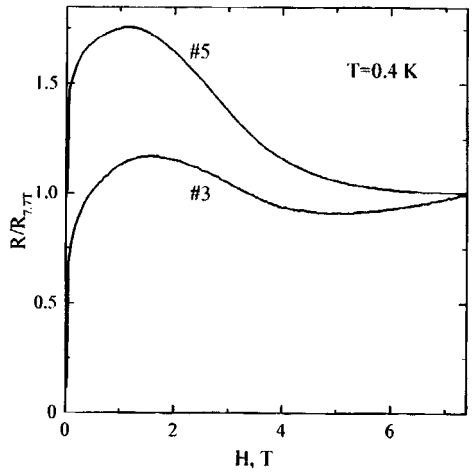

FIG. 2. Magnetic field dependences of the resistance in two different states (#3 and #5), $T=0.4$ K (compare with the temperature dependences $R(T)$ for the same states in Fig. 1).

reason, the very existence of a large magnetoresistance attests to the existence of a superconducting interaction, which is destroyed (or weakened) by a magnetic field, in a given state at a given temperature. For example, according to the inset in Fig. 1, the superconducting interaction in the state #2 first appears at 40 K and not 30 K, as one might conclude from the curve $R(T)$. In the most resistive state (#5) the $R(H)$ curve clearly exhibits manifestations of a superconducting interaction at $T=0.4$ K, while on the

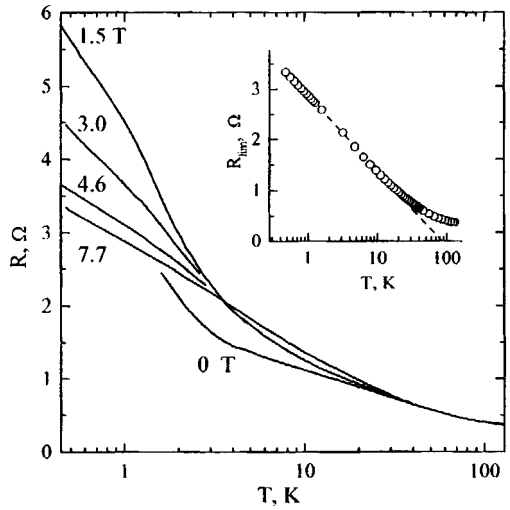

FIG. 3. Temperature dependences of the resistance in the state #5 in different magnetic fields. The limiting curve $R_{\rm lim}(\log T)$ (7.7 T field) is shown separately in the inset.

$R(T)$ curve these manifestations are masked by the increase in R with decreasing temperature.

All three components of the superconducting response can be distinguished in the curves $R(H)$ in Fig. 2. The rapid growth of the resistance in weak fields reflects the suppression of Josephson currents by a magnetic field; the region of negative slope $\partial R/\partial H$ reflects the growth of the single-particle current as a result of a decrease in the ratio Δ/T; and, finally, the positive derivative in strong fields for state #3 reflects the suppression of superconductivity in granules. The characteristic field H_{c2} is the same for the last two components, and the ratio between the components is determined by the temperature and structure of the sample: the average sizes and density of the superconducting granules as well as the transmittance of the contacts between them. It is known experimentally that the higher the normal-state resistance of the material, the larger the fraction of the incoherent component in the superconducting response.[9]

We now return to Fig. 3, where the curves $R(T)$ for the state #5 in different fields are presented. Even at our lowest temperature, 0.4 K, a 7.7 T field is already quite strong and the derivative $\partial R/\partial H$ in this field practically equals zero (see Fig. 2). We verified experimentally that $R(H)$ is saturated by 7.7 T at higher temperatures as well. This means that the curve $R(T)$ measured in a 7.7 T field is the limiting curve with respect to the family of such curves in weak fields: $R(T)_{7.7\,\mathrm{T}}=R_{\mathrm{lim}}(T)$. In the temperature range 4–30 K the family of curves approaches the limiting curve from below ($\partial R/\partial H>0$) and reaches the limiting values R_{lim} in fields of 1.5–2 T. For $T<4$ K the resistance R, increasing in weak fields, becomes much greater than R_{lim}, but the derivative $\partial R/\partial H$ changes sign in fields 1.5–2 T and becomes negative, so that the family approaches the limiting curve from above and reaches the curve in fields of 6–7 T.

In Fig. 3 the temperature is plotted on the abscissa in a logarithmic scale. In this scale the limiting curve $R(T)$ at $T<20$ K is a *straight line*. To underscore this basic experimental result of the present work, the curve $R_{\mathrm{lim}}(T)$ is once again plotted separately in the inset in Fig. 3. Such logarithmic temperature dependences have recently been observed in two other families of high-temperature superconductors — the systems $La_{2-x}Sr_xCuO_4$ (Refs. 10 and 11) and $Bi_2(Sr, La)_2CuO_{6+x}$ (Ref. 12). This is what motivated us to perform such an analysis of our results.

The physical mechanism leading to a logarithmic divergence in the low-temperature normal resistance of high-T_c superconductors is unclear at present. It should be noted that in the region of logarithmic temperature dependence the resistance varies by a factor of 4, i.e., the logarithmic term dominates. This signifies that weak-localization type processes cannot be responsible for the log T term. It is also difficult to invoke the Kondo effect to explain this dependence, since the curve $R_{\mathrm{lim}}(T)$ was measured in a quite strong field of 8 T, and similar curves were obtained in Refs. 10 and 11 even in a field of 60 T.

However, in this problem there are not only theoretical but also experimental ambiguities. Experiments must distinguish the dependence

$$\Delta R \propto \log T \tag{1}$$

from the dependences

$$1/R = a + bT^{1/n}, \quad n = 2 \text{ or } 3, \tag{2}$$

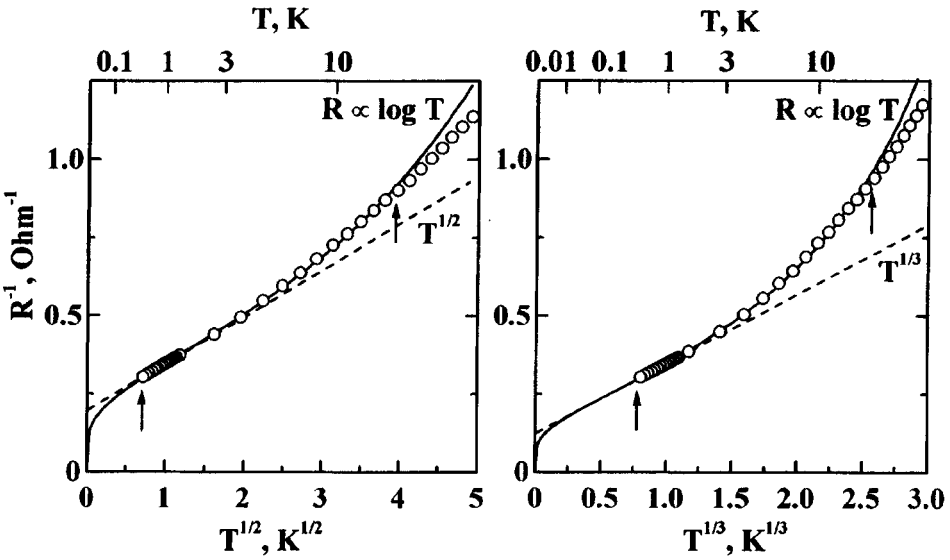

FIG. 4. Limiting values of the conductance $1/R_{\rm lim}$ as functions of $T^{1/2}$ and $T^{1/3}$. Solid line — description of the experimental data with the aid of log T. The arrows mark the temperature interval where this description agrees with experiment. The dashed straight lines demonstrate the region where the experimental data on $1/R_{\rm lim}$ can be described by a power-law function.

which follow from the scaling description of the neighborhood of the metal–insulator transition in a three-dimensional material[13] and have been repeatedly observed experimentally (see Ref. 14 and the references cited therein). Our results are presented in Fig. 4 in the scales $T^{1/2}$ and $T^{1/3}$. The temperature interval where the relation (2) describes the experimental data is narrower at the high-temperature end than in the case of relation (1). But at the low temperature end of the interval the differences in the descriptions (1) and (2) are smaller than the measurement accuracy, and it is obvious that even measurements performed on this sample at lower temperatures will not permit one to choose between these two descriptions. For this reason, experiments on other samples and materials must be performed in order to choose between the descriptions (1) and (2).

In summary, we have shown in experiments on the ceramic $NdBa_2Cu_3O_{6+x}$ that:

(a) The magnetoresistance (positive in weak fields and negative in strong fields) is much more sensitive to the presence of a superconducting interaction than is the function $R(T)$, and

(b) after superconductivity is destroyed by a magnetic field the temperature variations of the resistance below 20 K are described very well by the function log T.

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