Conductivity of the Hall effect in $YBa_2Cu_3O_{7-x}$ single crystals with different oxygen concentrations

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The effect of oxygen concentration in the single crystals of high-temperature superconductor $YBa_2Cu_3O_{7-x}$ on the electrical resistivity and the Hall effect in the plane perpendicular to the *c* axis has been studied.

Several experimental studies of the effect of oxygen concentration on the electrical and other properties of the high-temperature superconductor $YBa_2Cu_3O_{7-x}$ have now been published. The results of these studies based on polycrystalline samples synthesized by different methods are the same in general features but often differ markedly in details (see, e.g., Refs. 1–5).

We have studied the effect of oxygen concentration on the electrical properties of $YBa_2Cu_3O_{7-x}$ single crystal samples. The single crystals which we have studied were grown at the Institute of Crystallography of the Academy of Sciences of the USSR, by

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a method described elsewhere.[6] The single crystals are thin, naturally faceted wafers with the cross sections $\sim 1 \times 1$ mm^2 and thickness 0.02–0.04 mm. The plane of these single crystals is perpendicular to the major axis (the c axis) of the crystal. The measuring contacts were made from a conducting silver paste. The sample, along with the deposited contacts, was annealed in flowing oxygen at $T = 750$ °C for 12 hours and then cooled down to room temperature at the rate of 1 °C/min. The silver paste was brazed to the sample and the contacts thus obtained had a resistance of $\lesssim 1\Omega$. To further reduce the oxygen content, we annealed the samples in air at a temperature T_q. The cell containing the sample was then filled with helium and the sample was initially cooled rapidly to 350 °C at the rate of 200 °C/min and then it was cooled slowly down to room temperature, at the rate of 20 °C/min. A two-step cooling of this sort has, on the one hand, made it possible, in our view, to keep the oxygen concentration in the sample close to the equilibrium concentration at $T = T_q$, since at $T \lesssim 350$ °C the sample releases oxygen so slowly that it can be ignored and, on the other hand, the slow second step makes it possible to reduce the number of imperfections in the crystal.

Figure 1 shows the curves for the resistivity in the plane of the wafer $\rho_{\parallel}(T)$, measured by the four-contact method, using the same sample annealed at various, gradually rising values of T_q. The resistivity $\rho_{\parallel}$ (300 K) of the sample annealed in oxygen is ~ 200 $\mu\Omega \cdot$cm. The value of $\rho_{\parallel}$ was measured with $\sim 5\%$ relative error. Figure 2 shows the dependence on T_q of the superconducting transition temperature T_c and its width ΔT_c, measured from the decrease in the resistivity at the level 0.1–0.9. It follows from these curves that with an increase in T_q, $\rho_{\parallel}$ and T_c increase monotoni-

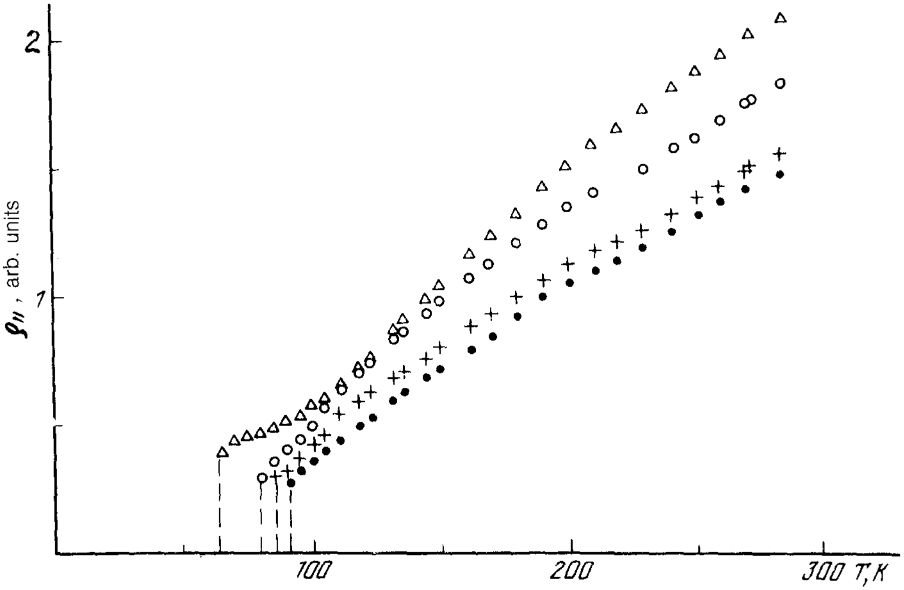

FIG. 1. Temperature dependence of the resistivity $\rho_{\parallel}(T)$ at various annealing temperatures T_q. ●—Sample annealed in oxygen; + —$T_q = 500$ °C; ○—$T_q = 550$ °C; Δ—$T_q = 600$ °C.

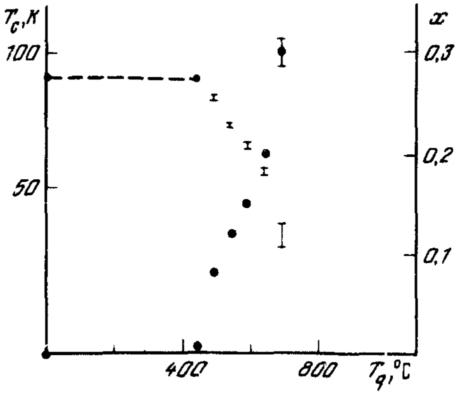

FIG. 2. T_c and oxygen concentration x(●) versus T_q.

cally and T_c decreases. There are two structural features which set our data apart from those obtained with polycrystalline samples, which were reported earlier (see, e.g., Ref. 4). First, the width of the superconducting transition in a single crystal is markedly narrower than that of the polycrystals, down to the temperatures $T_q \sim 700\,^\circ$C, at which T_c begins to vary rapidly with T_q (at $T_q \leqslant 450\,^\circ$C $\Delta T_c \lesssim 0.3$ K). This behavior suggests that the single crystals are homogeneous in the plane perpendicular to the c axis. Secondly, with an increase in T_q and, hence, a decrease in the oxygen concentration, the resistivity $\rho_{\parallel}$ of single crystals increases much slower than the resistivity of polycrystals. It is reasonable to assume that the dependence of T_c on the oxygen concentration x in polycrystal samples is the same as in single crystal samples. The value of x in one sample in this case can be crudely estimated from T_c and from the widely known $T_c(x)$ dependence, which has been reported in the literature. The plot of x versus T_q, determined from the data obtained by I. P. Zibrov and N. I. Romanova at the Institute of Crystallography, is shown in Fig. 2. We thus find that as T_c decreases from 92 K to 62 K, which corresponds to an increase in x from 0 to ~ 0.15, the resistivity $\rho_{\parallel}$ increases by $\sim 40\%$ (Fig. 1), whereas in polycrystals $\rho_{\parallel}$ increases severalfold.[3,4] This disagreement could be partially attributed to a decrease in the sample imperfection resulting from the two-step quenching used by us. Furthermore, according to the results of electron-microscopy studies,[7] the grains which make up the polycrystalline samples have defective layers directed perpendicular to the c axis. The presence of these defects should lead to an increase in T_c and possibly to an increase in ρ.

After a quenching at maximum T_q, the crystal was again annealed in flowing oxygen. As a result, T_c and $\rho_{\parallel}$ returned to the initial values, within an error of $\lesssim 10\%$, obtained from a sample annealed in oxygen. This behavior suggests that the measured values of $\rho_{\parallel}$ and T_c are attributable primarily to the oxygen concentration in the sample.

To determine whether the increase in the resistivity due to the decrease in the oxygen concentration is caused by the change in the number of carriers or the change in their mobility, we studied the Hall effect. The results of measurements of the Hall effect in the plane perpendicular to the c axis are shown in Fig. 3. The data shown in

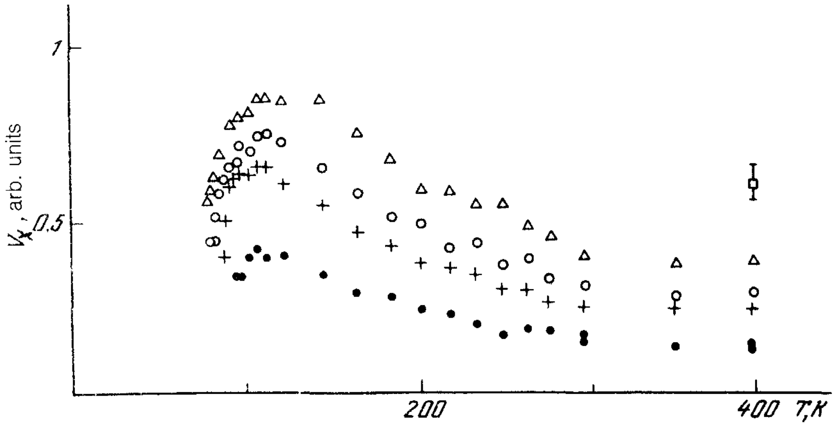

FIG 3. Temperature dependence of the Hall voltage V_X at various annealing temperatures T_q. ●—Sample annealed in oxygen; +—$T_q = 500\,^\circ\mathrm{C}$; ○—$T_q = 550\,^\circ\mathrm{C}$; Δ—$T_q = 600\,^\circ\mathrm{C}$; □—$T_q = 650\,^\circ\mathrm{C}$

Figs. 1 and 3 were obtained from the same sample. The Hall voltage, measured in $\mathbf{H}\|c$ fields up to 13 kOe, depends linearly on the field H and on the measuring current (~ 10 mA). The positive Hall constant measured in several crystals with $T_c \approx 92$ K is R_X (300 K) $\approx 10^{-3}$ cm^3/C within experimental error, which corresponds to the carrier density $n_{300} \approx 7 \times 10^{21} \pm 50\%$. These values are approximately equal to the results calculated in Ref. 8 and measured in $YBa_2Cu_3O_7$ single crystals[9] and ceramics[5].

The results of the measurements of the Hall effect and the resistivity are in qualitative agreement with each other: A decrease in the oxygen concentration leads to a decrease in the number of carriers n determined on the basis of a simple band model. The resistivity increases much faster, however, than the rate at which the carriers decrease. This behavior seems to suggest that there are various types of carriers, since otherwise this would suggest that their relaxation time would increase with decreasing oxygen concentration. This is a doubtful conclusion, since a decrease in the oxygen concentration is accompanied by an increase of the disorder in the arrangement of its atoms in the crystal.

There are two structural features in the behavior of the $V_X(T)$ curve: At $T_0 \approx 290$ K the shape of the $V_X(T)$ curve changes from that which is typical for metals, $V_X(T) = \text{const}$ at $T > T_0$, to a curve which increases monotonically at $T < T_0$, as the temperature is lowered, and the presence of a maximum on this curve at $T = 100$–120 K. At $T = T_0$ the slope of the curve changes less frequently as the oxygen concentration in the sample decreases, while the temperature T_0 remains constant. The $\rho_\|(T)$ curve has no structural features at the point T_0. The position of the maximum on the $V_X(T)$ curve shifts slightly up the temperature scale with decreasing oxygen concentration. At temperatures close to the position of the maximum (~ 100–120 K) the $\rho_\|(T)$ curve for samples annealed in oxygen was found in Ref. 10 to deviate from linear behavior (its slope increased).

Six crystals were used to study the Hall effect. The indicated characteristic features were observed in all crystals with $T_c \approx 92$ K. At a temperature T_0 no structural feature was observed in one of the samples with $T_c = 82$ K after it was annealed in oxygen, which seems to suggest that annealing has affected its quality adversely. The Hall voltage decreased monotonically after reaching the peak value at $T = 110$ K. At $T \lesssim 300$ K, R_X in this case was severalfold higher than in good crystals.

The presence of Hall voltage, which indicates that at $T < T_0$ the carriers increase in number, was previously pointed out by Gorlova *et al.*,[9] who attributed it either to the development of the Peierls instability or to the antiferromagnetic ordering. The currently available experimental data are, in our view, insufficient for an unambiguous interpretation of these structural features.

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