Effect of oxygen content on the electrical properties of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ single crystals

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Abstract. The effect of oxygen content in the single crystals of high-temperature superconductor $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ on the electrical resistivity, the Hall effect in the plane perpendicular to the c axis and the energy gap Δ , measured with tunnelling electron microscope, has been studied. The distribution of the gap along the surface of the crystal was also studied. The results of the study on the relationship between the magnitude of the energy gap Δ and the superconducting transition temperature T_c of single crystals with various oxygen contents are approximated by the linear dependence $2\Delta_{av} = 4.4 kT_c$.

Keywords. Superconductivity; $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$; electrical properties; tunnelling microscopy.

1. Introduction

Considerable experimental studies were devoted to investigation of the effect of oxygen content on the electrical and other properties of HTSC $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$. Such studies were based principally on polycrystalline samples (see e.g. Cava *et al* 1987; Monod *et al* 1987; Mydosh 1987; Sawada *et al* 1987; Wang *et al* 1987), although some data on single crystals have appeared recently (see e.g. Kotyuzhanski 1988; Aleksandrov *et al* 1988; Volodin *et al* 1988; Barabanenkov *et al* 1989).

Since the earlier results show similarity in general features but differ markedly in details, it was of interest to study the effect of oxygen content on the basic parameters of HTSC $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ viz resistivity, number of carriers and energy gap. The oxygen content in HTSC can easily be varied by annealing them in an appropriate atmosphere.

2. Procedure and samples

The data on the number of carriers in the investigated samples were obtained by studying the Hall effect. To measure the resistivity ρ and the Hall voltage V_H , the measuring contacts from a conducting silver paste were deposited on the crystals. The Hall voltage was measured in the basal plane of the crystal in $H \parallel c$ fields to 13 kOe at the measuring current $I \leq 10$ mA.

The energy gap of the HTSC was determined from the current-voltage characteristics obtained from a tunnelling electron microscope (TEM) (Kirtley *et al* 1987; Volodin and Khaikin 1987). Because of the unique spatial localizability of the measurements, TEM can be used to find the profile of the energy gap along the surface of superconducting single crystals (Volodin and Khaikin 1987). The tunnelling measurements were carried out in the undamaged central region of a single crystal at $T = 4.2$ K.

Since the surface layer of the sample becomes non-conducting at a temperature $T \sim 4$ K, we used a procedure (Volodin and Khaikin 1987) involving the use of a needle

of the TEM at liquid-helium temperature to destroy this layer in order to obtain a vacuum tunnelling current $I_T \sim 1$ nA and reproducible tunnelling I – V characteristics. The derivatives of the I – V characteristics were measured at different points of the sample at intervals of 10^3 Å. Although the effective region through which the vacuum tunnelling current flows is ~ 1 – 10 Å, we chose such a large distance between the measurement points to prevent the needle from striking a section of the crystal surface which was damaged by the preceding measurement. The average value of the gap width, Δ_{av} , was determined from the results of the measurements of an area of size $\sim 1 \mu\text{m}^2$. Such measurements of the test samples were carried out in ten different areas.

The $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ single crystals were grown at our Institute by a method described by Bykov *et al* (1988). These single crystals are thin, shiny, black wafers with characteristic dimensions $1 \times 1 \times 0.03$ mm. The large faces of the wafer are natural (001) faces.

The sample along with the deposited contacts was initially annealed in flowing oxygen at $T = 1020$ K for 12 h and then cooled at 1 K/min. The silver paste was brazed to the sample and the contacts thus obtained had a resistance of $\leq 1 \Omega$. To gradually reduce the oxygen content and the corresponding T_c , we annealed the samples in air for 5 h at a certain temperature T_q , which increased from one experiment to another. The cell containing the sample was then filled with helium and the sample cooled rapidly to 620 K at 200 K/min and then slowly to room temperature at 20 K/min. A two-step cooling of this sort has, on the one hand, made it possible, in our view, to keep the oxygen content in the sample close to the equilibrium concentration at $T = T_q$, since at $T \lesssim 620$ K 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. The change in the oxygen content, x , in samples was detected from the change in T_c and was determined from widely known dependence $T_c(x)$, which, as was shown earlier (Cava *et al* 1987; Aleksandrov *et al* 1988), differs negligibly in polycrystal and single-crystal samples.

3. Experimental results

Figure 1 shows the resistivity curves in the plane of the wafer $\rho_{||}(T)$, measured by the four-contact method, using the same sample annealed at various, gradually rising values of T_q . The resistivity $\rho_{||}(300 \text{ K})$ of the sample annealed in oxygen is $\sim 200 \mu\Omega\cdot\text{cm}$. The value of $\rho_{||}$ 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 increase in T_q , $\rho_{||}$ and ΔT_c increase monotonically 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. Monod *et al* 1987). First, the width of the superconducting transition in a single crystal is markedly narrower than that of the polycrystals, up to the temperatures $T_q \sim 970$ K, at which T_c begins to vary rapidly with T_q (at $T_q \leq 720$ K $\Delta T_c \lesssim 0.3$ K). This behaviour 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 content, the resistivity $\rho_{||}$ of single crystals increases much slower than the resistivity of polycrystals.

The plot of x versus T_q , determined from our data and from the dependence of $T_c(x)$

Figure 1. Temperature dependence of the resistivity $\rho_{||}(T)$ at various annealing temperatures T_q . ●—Sample annealed in oxygen; +— $T_q = 770$ K; O— $T_q = 820$ K; Δ — $T_q = 870$ K.

(Cava *et al* 1987), is shown in figure 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 , $\rho_{||}$ increases by $\sim 40\%$ (figure 1), whereas in polycrystals $\rho_{||}$ increases several-fold (Sawada *et al* 1987; Monod *et al* 1987). 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 (Nakahara *et al* 1987), 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 ΔT_c and possibly to an increase in ρ . It is interesting to note that the conductivity in the basal plane changes with changing oxygen content and with a simultaneous decrease in T_c , from a metallic (at $T_c \gtrsim 60$ K) to a semiconductor conductivity (at $T_c \lesssim 60$ K).

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

The results of measurements of the Hall effect in the plane perpendicular to the c axis are shown in figure 3. The data shown in figures 1 and 3 were obtained from the same sample. The Hall voltage depends linearly on the field H and on the measuring current I in the whole interval of variations of H and I . The positive Hall constant measured in several crystals with $T_c \approx 92$ K is $R_x(300 \text{ K}) \approx 10^{-3} \text{ cm}^3/\text{C}$ 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 by Allen *et al* (1987) and measured in $\text{YBa}_2\text{Cu}_3\text{O}_7$ ceramics (Wang *et al* 1987) and single crystals (Gorlova *et al* 1988).

Figure 4 shows one of the results of the measurement of the energy gap profile along the surface of a single crystal with $T_c \approx 54$ K. The magnitude of the gap, measured in MeV, is indicated by the height at which the points above the nodes of the x, y reference grid are situated. The points are connected by line segments to help depict the $\Delta(x, y)$

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

Figure 3. Temperature dependence of the Hall voltage V_H at various annealing temperatures T_q : ● — Sample annealed in oxygen; + — $T_q = 770$ K; ○ — $T_q = 820$ K; Δ — $T_q = 870$ K; □ — $T_q = 920$ K.

Figure 4. Distribution of the energy gap Δ along the surface of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ single crystal with $T_c = 54$ K.

Figure 5. Average width of the energy gap Δ_{av} versus the critical temperature T_c .

surface. Such a topogram of the profile of the Δ values shows that the superconducting properties of the surface of the single crystal are sufficiently uniform. It also shows, however, that the surface has regions where the value of Δ differs by a factor of ~ 1.5 . The topograms are devoid of non-superconducting regions.

Figure 5 is a plot of the $\Delta_{av}(T_c)$ curve for one of the samples after subjecting it to repeated annealing which changes its T_c . The vertical and horizontal segments near the points on the plot of $\Delta_{av}(T_c)$ characterize respectively the spatial scatter in Δ and the width of the superconducting transition ΔT_c , which was measured from the $\rho_{||}(T)$ curve. Taking into account the scatter in the parameters shown in the plot, we can describe the relationship between them by the linear relation $2\Delta_{av} = (4.4 \pm 0.1) kT_c$.

4. Discussion of results

The results of the measurements of the Hall effect and the resistivity are in qualitative agreement with each other: A decrease in oxygen content 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 behaviour seems to suggest that there are various types of carriers, since otherwise this would suggest that their relaxation time would increase with decreasing oxygen

content. This is a doubtful conclusion, since a decrease in the oxygen content is accompanied by an increase of the disorder in the arrangement of its atoms in the crystal.

There are two structural features in the behaviour of the $V_H(T)$ curve: At $T_1 \approx 290$ K the shape of the $V_H(T)$ curve changes from that which is typical for metals. $V_H(T) = \text{const}$ at $T > T_1$, to a curve which increases monotonically at $T < T_1$, as the temperature is lowered, and the presence of a maximum on this curve at $T_2 \approx 100$ – 120 K. At $T = T_1$ the slope of the curve changes more sharply as the oxygen content in the sample decreases, while the temperature T_1 remains constant. The $\rho_{\parallel}(T)$ curve has no structural features at the point T_1 . The position of the maximum on the $V_H(T)$ curve shifts slightly up the temperature scale with decreasing oxygen content. At temperatures close to T_2 the $\rho(T)$ curve for samples annealed in oxygen was found by Kotyuzhanskii and Svistov (1988) to deviate from linear behaviour (its slope increased).

The presence of temperature T_1 , below which the $V_H(T)$ -dependence indicates that at $T < T_1$ the carriers decrease in number, was previously pointed out by Gorlova *et al* (1988), 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.

The change in the nature of the conductivity, detected by us in crystals with $T_c \lesssim 60$ K, was observed many times before in ceramic samples by various investigators. One plausible explanation of this phenomenon is based on the assumption that the structure of the samples is granular in nature. Under this assumption the samples would be comprised, because of the non-uniform oxygen distribution, for example, of "good" superconducting regions with a metallic conductivity and "bad" non-superconducting regions with a semiconductor conductivity. Such a structure can also take place in single crystals with low oxygen content (Barabanenkov *et al* 1989; Molchanov *et al* 1989). Although single crystal samples theoretically can have a non-uniform distribution of oxygen and a mechanism which was described above and which accounts for the semiconductor nature of the conductivity, the data of tunnelling measurements presented in figure 4 fail to confirm this possibility. They seem rather to suggest that the $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ system, in which localization is observable, can undergo a transition to the superconducting state.

The proportional dependence of Δ_{av} on T_c (figure 5) makes it possible to conclude that the carrier pairing mechanism in $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ does not change considerably over the range of variation of x being studied (from 0 to ~ 0.3).

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