Energy gap in $YBa_2Cu_3O_{7-x}$ single crystals with various oxygen concentrations

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(Submitted 2 September 1988)
Pis'ma Zh. Eksp. Teor. Fiz. **48**, No. 8, 457–460 (25 October 1988)

A tunneling electron microscope has been used to study the relationship between the magnitude of the energy gap Δ and the superconducting transition temperature of $YBa_2Cu_3O_{7-x}$ single crystals with various oxygen concentrations. The distribution of the gap along the surface of the crystal was also studied. The results of the study are approximated by the linear dependence $2\Delta_{av} = 4.4\ kT_c$.

The first experimental studies of high-temperature superconductivity have clearly shown that the oxygen content decisively affects the electrical properties of high-T_c superconductors $YBa_2Cu_3O_{7-x}$ and primarily the critical temperature T_c (Ref. 1). The oxygen concentration in high-T_c samples can easily be varied by annealing them in an appropriate atmosphere. The results of several such studies involving principally ceramic samples (see, e.g., Refs. 2 and 3) and also single crystal samples have recently been published.[4]

It is thus clearly of interest to determine the size of the energy gap Δ and its spatial distribution in the single crystals of high-T_c $YBa_2Cu_3O_{7-x}$ superconductors with various oxygen concentrations and to find the relationship between the energy gap Δ and the superconducting transition temperature.

The $YBa_2Cu_3O_{7-x}$ single crystals were grown at the Institute of Crystallography, Academy of Sciences of the USSR by a method described in Ref. 5. These single crystals are thin, shiny, black wafers with characteristics dimensions $1 \times 1 \times 0.03$ mm. The large faces of the wafer are natural (001) faces. The superconducting transition temperature T_c is determined from the temperature dependence of the resistivity in the basal plane of the crystal, $\rho_{\parallel}$, which was measured by the four-contact method. The contact surfaces were deposited on the sample by brazing a conducting silver paste to it.

The sample along with the deposited contacts was initially annealed in flowing oxygen at $T = 1020$ K for 12 h and then cooled at the rate of 1 K/min. To gradually reduce the oxygen concentration 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 was cooled rapidly to 620 K at the rate of 200 K/min and then slowly to room temperature at the rate of 20 K/min. The change in the oxygen concentration was detected from the change in T_c (Ref. 4).

The energy gap of the high-T_c superconductor was determined from the current-voltage characteristics obtained from a tunneling electron microscope.[6,7] Because of the unique spatial localizability of the measurements, the tunneling electron microscope can be used to find the profile of the energy gap along the surface of superconducting single crystals.[7] The tunneling measurements were carried out in the undamaged central region of a single crystal at $T = 4.2$ K.

As the measurements with the tunneling electron microscope have shown, at room temperature the conductivity of the surface of a $YBa_2Cu_3O_{7-x}$ single crystal is of a semiconductor nature: To obtain an appreciable tunneling current ($I_T \sim I$ nA), a voltage on the order of 5 V had to be applied to the tunneling gap. Since the surface layer of the sample becomes nonconducting at a temperature $T \sim 4$ K, we used a procedure involving the use of a needle of the tunneling electron microscope[7] at liquid-helium temperature to destroy this layer in order to obtain reproducible tunneling I-V characteristics. The needle of the tunneling electron microscope, which was initially introduced into the nonconducting surface layer until a current of I nA was attained in it, was withdrawn from the sample a distance of ~100 Å and then again brought near it until a vacuum tunneling current $I_T \sim I_{\mathrm{nA}}$ was measured in it. The energy gap was deduced from the derivatives of the I-V characteristics using a method described in Ref. 7. The derivatives of the I-V characteristics were measured at different points of the sample at intervals of 1000 Å. Although the effective region through which the vacuum tunneling current flows is ~1–10 Å, we chose such a large distance between the measurement points in order to prevent the needle from striking a section of the crystal surface which was damaged by the preceding measurement. A typical example of the derivatives of the I-V characteristics for four adjacent points at the surface of the sample with $T_c \approx 54$ K is shown in Fig. 1. The I-V characteristics of the samples with $T_c \approx 93$ K were defined much more clearly. By analogy with the case in which the samples were completely saturated with oxygen, the gap width of the samples with a lower T_c was determined from the first pronounced peak on the I-V characteristics. The average value of the gap width, Δ_{av}, was determined from the results of the measurements of an area of size ~1 μm^2. Such measurements of the test samples were carried out in ten different areas.

We should note that the I-V characteristics exhibit a pronouced asymmetry. This asymmetry was reported in the first experimental studies of high-T_c superconductors with use of a tunneling electron microscope.[6,7] The nature of this phenomenon, however, has not yet been explained.

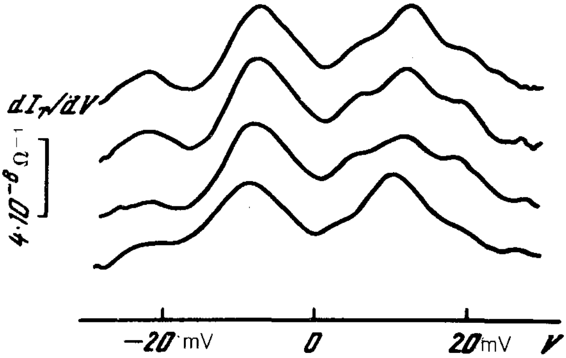

FIG. 1. The derivatives of the current-voltage characteristics, measured by means of a tunneling electron microscope, at four adjacent points of a $YBa_2Cu_3O_{7-x}$ single crystal with $T_c \approx 54$ K.

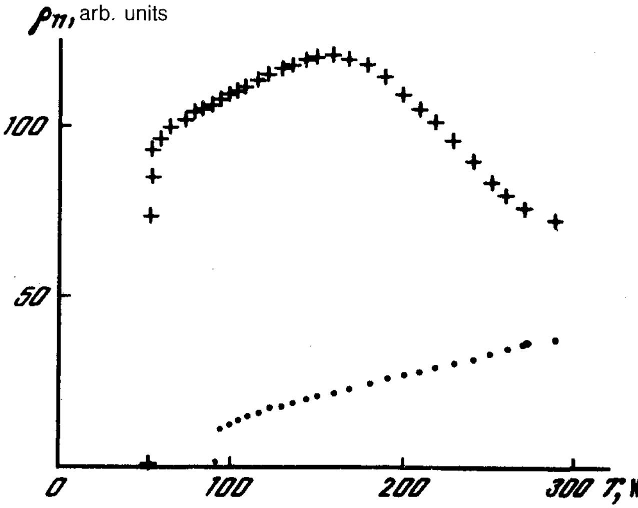

FIG. 2. Temperature dependence of the resistivity $\rho_{\|}$ at various annealing temperatures T_q. ●—Sample annealed in oxygen; +—sample annealed at $T_q = 970$ K.

Figure 2 shows two typical $\rho_{\|}(T)$ curves plotted for one of the samples. It is interesting to note that the conductivity in the basal plane changes with changing oxygen concentration and with a simultaneous decrease in T_c, from a metallic conductivity (at $T_c > 60$ K) to a semiconductor conductivity (at $T_c \lesssim 60$ K). Such a change in the nature of the conductivity 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 nonuniform oxygen distribution, for example, of "good" superconducting regions with a metallic conductivity and "bad" nonsuperconducting regions with a semiconductor conductivity.

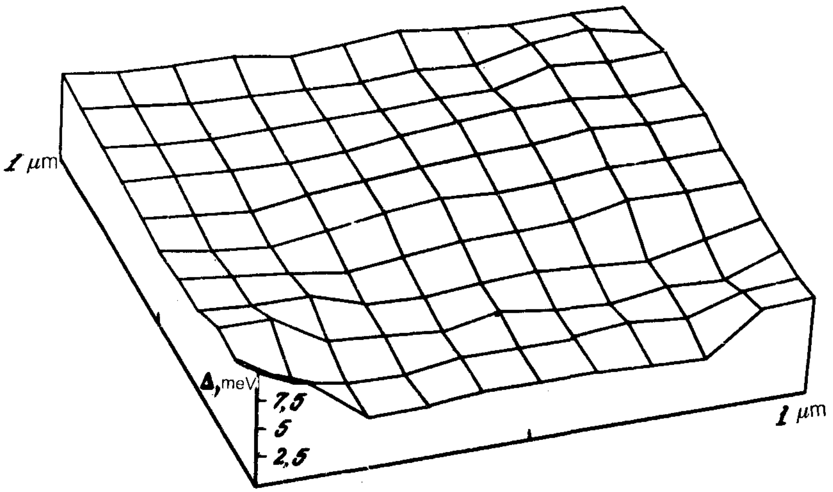

FIG. 3. Distribution of the energy gap Δ along the surface of $YBa_2Cu_3O_{7-x}$ single crystals with $T_c = 54$ K.

Figure 3 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 $\Delta(x,y)$ 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 nonsuperconducting regions.

Although single crystal samples theoretically can have a nonuniform distribution of oxygen and a mechanism which was described above and which accounts for the semiconductor nature of the conductivity, the data presented here fail to confirm this possibility. They seem rather to suggest that $YBa_2Cu_3O_{7-x}$ system, in which localization is observable, can undergo a transition to the superconducting state.

Figure 4 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 resistive superconducting transition, which was measured from the 0.1–0.9 level on the $\rho_{\parallel}(T)$ curve. Taking into account the scatter in the parameters shown in the plot, we can describe the relationship between them by the linear relation $2\Delta_{av} = (4.4 \pm 0.1)kT_c$. We see from this result that the pairing mechanism of the $YBa_2Cu_3O_{7-x}$ system changes only slightly over the range of variation of x being studied [from 0 to ~ 0.3 (Ref. 4)].

It would have been of interest to study the $\Delta(T_c)$ dependence for crystals with a lower oxygen concentration. However, after repeated annealing based on the adopted procedure, the single crystal formed on its surface a thick, nonconducting layer of a matte finish, which prevented us from carrying out this study.

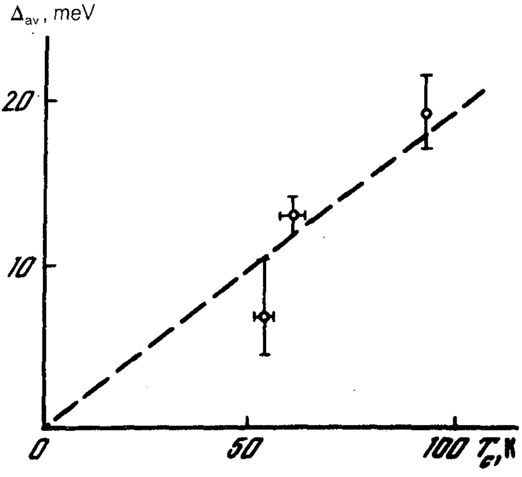

FIG. 4. Average width of the energy gap Δ_{av} versus the critical temperature. T_c.

We wish to thank S. M. Stishov and M. S. Khaĭkin for interest in this study and for a discussion of the results. We also thank A. B. Bykov and O. K. Mel'nikov for furnishing the single crystals.

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Translated by S. J. Amoretty