Ground state of the superconducting compound $YBa_2Cu_3O_x$ at $x<6.5$

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A study has been made of how the superconducting properties of $YBa_2Cu_3O_x$ single crystals are affected by a low-temperature annealing under conditions which rule out a loss of oxygen. A sufficiently long annealing completely erases the superconductivity of $YBa_2Cu_3O_x$ at $x < 6.5$. Tunneling measurements carried out for a superconducting single crystal with $x \approx 6.32$ showed that the gap feature on the current-voltage characteristic is observed over only $\sim 60\%$ of the area of the sample. It is confirmed that the ground state of $YBa_2Cu_3O_x$ at $x < 6.5$ is an insulating state.

Correlation effects are known to cause the electron spectrum of the divalent-copper compound La_2CuO_4 to acquire the characteristics of an insulator. Correspondingly, it has been expected that the compound $YBa_2Cu_3O_{6.5}$, with a formal copper valence of 2, would also be an insulator.[1] Nevertheless, there are reports in the literature (e.g., Ref. 2) which indicate a manifestation of superconducting properties at compositions $x \leqslant 6.5$ and the absence of any structural features at the point $x = 6.5$. It was emphasized in Ref. 3, however, that the superconducting properties of the com-

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pound $YBa_2Cu_3O_x$ at $x < 6.5$ are extremely sensitive to the history of the sample. In the same paper it was suggested that the superconductivity of $YBa_2Cu_3O_x$ at $x < 6.5$ is "extrinsic," stemming from a nonuniform oxygen distribution.

In the present letter we are reporting a study of the dependence $T_c(x)$, where T_c is the critical temperature, for the compound $YBa_2Cu_3O_x$. We used single-crystal samples with various oxygen concentrations, which were rendered homogeneous through a low-temperature annealing in helium. We are also reporting on the tunneling characteristics of a $YBa_2Cu_3O_x$ single crystal with $x = 6.32$.

For the present experiments we used single-crystal samples of $YBa_2Cu_3O_x$ with various oxygen concentrations, which were synthesized in the course of the studies reported in Ref. 3. The superconducting transition temperature was detected by a contactless method, in which we monitored the variation of the frequency of an *LC* oscillator whose inductance coil surrounded the test sample.[3]

The selected samples were studied by an x-ray method in order to determine the parameters of the unit cell. After their superconducting properties were studied, the samples were transferred to a hermetically sealed oven, which was filled with helium. They were heated at $T \leqslant 400$ °C for several hours and then cooled at 1 deg/min. After this procedure, the measurement cycle was repeated, and the samples were reannealed. Preliminary experiments revealed that the overall amount of oxygen in the samples was not affected, within ± 0.01 mole unit, by this procedure. The oxygen concentration was monitored by observing the parameters of the unit cell.

The experiments showed (Fig. 1) that a low-temperature annealing either has no effect on, or improves the quality of, the superconducting transition at $x > 6.5$, but at $x < 6.5$ it degrades the superconductivity to some extent, up to the point that it completely erases the superconductivity. The $T_c(x)$ dependence found is shown in Fig. 2. We see from Fig. 2 that the superconducting transition temperature changes essentially abruptly from 0 to $T \approx 55$ K in a narrow interval of oxygen concentrations in the region $x \approx 6.5$ (the absolute oxygen concentration was determined within ± 0.05 mole unit). In the normal phase, the samples with $x < 6.5$ exhibit a nonmetallic temperature dependence of the electrical conductivity in the *ab* plane.

Before we move on to a discussion, we will also report the results of some tunneling experiments which were carried out on a $YBa_2Cu_3O_x$ sample with $x = 6.32$. This

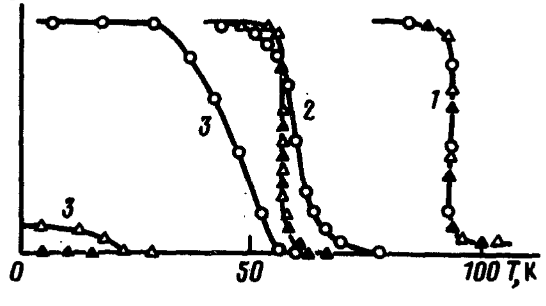

FIG. 1. Superconducting transition in $YBa_2Cu_3O_x$ single crystals according to the results of contactless measurements ($\Delta\omega$ is the change in the frequency of the *LC* oscillator). The oxygen concentrations (x) in the samples were: 1–7.0; 2–6.6; 3–6.44. O) Data for the original samples; △) after a single annealing in helium; ▲) after a repeated annealing (see the text proper).

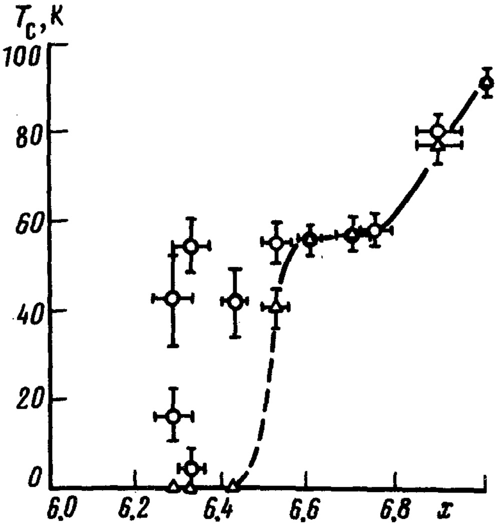

FIG. 2. Superconducting transition temperature T_c versus the oxygen concentration x. ○—Data for the initial samples; △—after annealing in helium.

sample, which was typical of the initial lot of single crystals, was not subjected to any sort of processing after growth. Contactless measurements showed that this sample exhibited a diffuse superconducting transition ($T_c \approx 35$–65 K). Using a scanning tunneling microscope at $T = 4.2$ K, we studied several regions 1×1 μm in size on the surface of the sample in the ab plane. At each of 81 points separated from each other by ~1000 Å in this region we measured the tunneling current-voltage characteristics. The procedure followed before the measurement of the current-voltage characteristics was similar to that described in Ref. 4. It consisted of using the needle of the scanning tunneling microscope to damage the thin nonconducting surface layer on the crystal at $T = 4.2$ K and then bringing the needle up to the exposed surface of the superconductor until a given vacuum-tunneling current, ~1 nA, was attained (at a voltage ~100 mV). The energy gap was found from the maxima of the derivatives of the current-

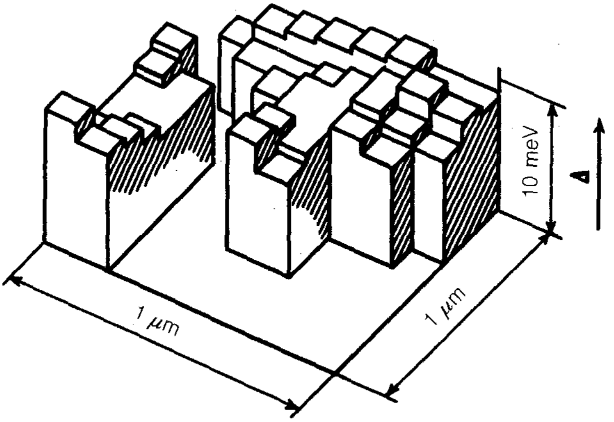

FIG. 3. Distribution of the energy gap Δ along the surface of a "quenched" $YBa_2Cu_3O_x$ single crystal according to tunneling microscopy (diagram).

voltage characteristics. We wish to stress that only $\sim 60\%$ of the current-voltage characteristics obtained exhibit a gap feature ($\Delta_{av} = 7.9$ meV; Fig. 3). This result is in complete agreement with our conclusion that the oxygen is distributed nonuniformly in superconducting $YBa_2Cu_3O_x$ samples with $x < 6.5$. When we allow for the uncertainty in the transition temperature, we conclude that the value of the parameter $2\Delta_{av}/kT$ agrees with the BCS theory. This question will be studied in more detail in another publication.

Let us go back to the $T_c(x)$ curve in Fig. 2. The point (or region) in which the superconductivity arises abruptly ($x = 6.5$) corresponds to a formal copper valence of 2. In this situation an identification of the observed feature with a Mott-Hubbard transition would seem extremely plausible. According to the Hubbard model, the metallic conductivity and the superconductivity of $YBa_2Cu_3O_x$ result from a doping of the "starting" composition $YBa_2Cu_3O_{6.5}$. However, the obvious asymmetry of the doping effect apparently indicates that the hybridization of the *d* states of copper and the *p* states of oxygen is not complete. It may be that the electronic states associated with the *d* orbitals of copper are localized, at least at $x < 6.5$. If the situation remains the same at $x > 6.5$, the superconductivity of $YBa_2Cu_3O_x$ should be linked primarily with *p* states of oxygen.[5,6]

These arguments cast doubt on a linkage of the abrupt onset of superconductivity with the appearance of a Hubbard state. The most likely suggestion is that a Hubbard splitting of electronic states of copper in the CuO_2 planes occurs at any oxygen concentration. In this connection, the "starting" state could more plausibly be identified as $YBa_2Cu^{I}Cu_2^{II}O_6$, containing copper with different valences, and an explanation of the features on the $T_c(x)$ diagram should be sought in the specific behavior of the doping effect of the CuO chains and their fragments as a function of the concentration[1)] (Ref. 7).

We wish to thank our co-authors in Ref. 3 for permission to use the corresponding samples. We also thank M. S. Khaĭkin and I. B. Al'tfeder for interest and assistance in this study.

[1)] Aside from the obvious features on the $T_c(x)$ diagram at $x = 6.5$ and 6.75, we should also call attention to the concentration of 6.25: Up to this concentration, the appearance of a superconductivity is still possible (Fig. 2). At the same value of *x*, the parameter *c* of the unit cell begins to decrease rapidly.[3]

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