New data on the dependence of the critical temperature on the oxygen concentration in the superconducting compound $YBaCu_3O_x$

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The superconducting and structural properties of $YBa_2Cu_3O_x$ single crystals with various oxygen concentrations have been studied. The nature of the transition to the superconducting state suggests that the oxygen is distributed nonuniformly in the samples with $x < 7$. The $T_c(x)$ curve is found to behave irregularly at $x < 6.5$.

In the present letter we report the result of an experimental study of the superconducting and structural properties of the compound $YBa_2Cu_3O_x$ with various oxygen concentrations. In contrast with the preceding studies (see, e.g., Ref. 1), this study was carried out using single crystal samples.

The $YBa_2Cu_3O_x$ single crystals were grown from a nonstoichiometric melt using a method described in Ref. 2. For the experiments we selected approximately 200 crystals of total mass ~ 70 mg and average dimensions $1.5 \times 1.5 \times 0.03$ mm. All these crystals have a tetragonal symmetry and the parameter values of the unit cell of the original samples are $a = 3.860\ (2)$ Å and $c = 11.81\ (1)$ Å. The selected crystals were placed on a balance of a thermogravimetric device and annealed to a constant mass in oxygen atmosphere at $p \approx 1$ atm and $T \approx 723$ K. The samples were then cooled at a rate ~ 1 deg/min. An increase in the mass of the crystals during oxygen saturation corresponds to a change in the concentration $\Delta x = 0.664 \pm 0.001$. X-ray structural analysis, which included the filling of the positions of the atoms, has made it possible to

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determine the chemical composition of the original crystals and those saturated with oxygen: $YBa_2CU_3O_{6.24(7)}$ and $YBa_2Cu_3O_{6.97(4)}$, in agreement with the thermogravimetric data. It was assumed, therefore, that $x = 7.0$ in the case of "saturated" crystals.

To obtain samples with an intermediate oxygen concentration, we held the entire lot of crystals at a temperature in the range 723–923 K in helium atmosphere with a continuous monitoring of the change in mass. When the mass loss of the crystals reached a level corresponding to $\Delta x = -(0.05\text{–}0.1)$, the samples were cooled rapidly to $T \approx 653$ K and annealed at this temperature for 2 hours. Ten single crystals were then selected randomly from the lot and the procedure was repeated. At the concentration level $x \lesssim 6.4$ the oxygen was removed from the samples in a vacuum of $\sim 1 \times 10^{-3}$ torr. X-ray diffraction study of the randomly chosen test single crystals showed that the parameters of the unit cell of single samples are nearly the same for the samples from the same lot. Consequently, these crystals contain the same amount of oxygen. The unit cell parameters of the single crystals were determined from the positions of the 200, 020, and 006 reflections, using a two-circle diffractometer.

The results of thermogravimetric and x-ray diffraction studies of the test crystals are shown in Fig. 1. Also shown in this figure is a plot of the data for two individual crystals which had sequentially gone through all the stages of processing described above. In the region $x \lesssim 6.4$ the removal of oxygen from individual samples was carried out in flowing helium, rather than in a vacuum, at a temperature lower than the usual temperature. As can be seen in Fig. 1, this procedure leads to an expansion of the existence domain of the orthorhombic phase down the x scale. We note one more

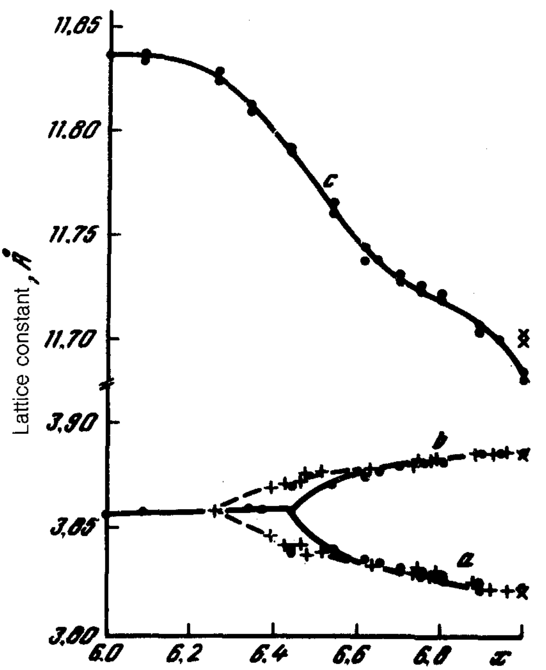

FIG. 1. Lattice constants of $YBa_2Cu_3O_x$ single crystals versus the oxygen concentration x. ●, ×—Results of study of the test crystals; the oxygen concentration was determined from the thermogravimetric data; ×—results obtained immediately after the oxygen saturation of the samples; +—data for two individual crystals; the oxygen concentration values $x < 6.4$ were obtained by annealing the samples in a flowing helium (see the text proper); the oxygen concentration was estimated from the values of the lattice constant c.

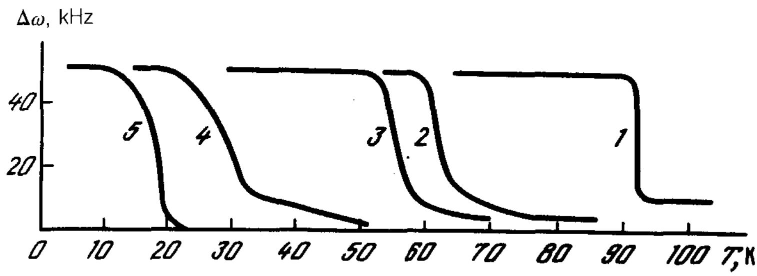

FIG. 2. Experimentally measured dependence of the frequency shift $\Delta\omega$ of the LC oscillator in the superconducting transition in the $YBa_2Cu_3O_x$ single-crystal samples. For curves 1–5 the oxygen concentrations x are 7.0, 6.77, 6.62, 6.51, and 6.41, respectively.

important circumstance. The unit cell parameters which were measured immediately after oxygen saturation of the crystals had the values $a = 3.822(2)$, $b = 3.888(2)$, and $c = 11.703(6)$ Å. The second measurements carried out several days later showed that the parameter $c = 11.688(6)$ decreased substantially, while the values of a and b remained essentially the same. Such relaxation was not observed at $x < 7$, apparently because of aging of the samples as a result of the removal of oxygen.

The superconductivity of $YBa_2Cu_3O_x$ single crystals was studied using an LC oscillator operating at a frequency $\omega_0 \approx 10$ MHz. Insertion of the sample into an induction coil of the oscillator caused a frequency shift $\Delta\omega$. In the case of small samples ($\Delta\omega \ll \omega_0$) this frequency shift is related to the resistivity of the sample by the relation $\rho \sim ((\Delta\omega_0/\Delta\omega(T)) - 1)^{1/2}$, where $\Delta\omega_0$ is the maximum frequency shift which occurs as a result of the total displacement of the rf field from the sample. The crystals to be studied were oriented in such a manner that the currents induced in them would flow in the (001) plane. The induction coil with the sample was placed in liquid-helium vapor and the temperature was measured with a copper-constantan thermocouple. To avoid overheating the sample due to the rf currents, we operated the oscillator in the pulsed mode. Typical curves of $\Delta\omega(T)$ obtained for the same crystal are shown in Fig. 2.

Figure 3 shows the results of the measurements of the superconducting-transition temperature T_c, carried out simultaneously for ten test crystals. These results represent the average behavior of the function $T_c(x)$. Also shown in Fig. 3 are some corresponding data for two individual crystals (Fig. 1). As can be seen in Fig. 3, all these data are basically in good agreement in the region $6.5 \lesssim x \lesssim 7$. In this entire region, except at the point $x = 7$, the superconducting transition occurs over a broad temperature range, presumably because of the nonuniform distribution of oxygen even in an individual single crystal.[3,4] At the same time, it should be noted that the method of synthesizing the samples has a marked effect on the functional dependence $T_c(x)$ when $x \lesssim 6.5$.

The following conclusions can be drawn from the results of these studies:

1. The oxygen concentration corresponding to the transition of the $YBa_2Cu_3O_x$

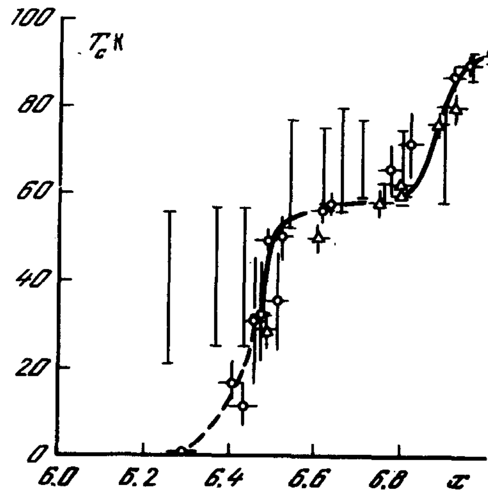

FIG. 3. The superconducting transition temperature of $YBa_2Cu_3O_x$ single crystals versus the oxygen concentration x. The vertical bars are the results of the "group" measurements; for $x < 6.45$ the crystals have a tetragonal symmetry; O, Δ—data for individual crystals; the same crystals were tested as those in the x-ray diffraction experiment (Fig. 1); for $x < 6.45$ the crystals retain the orthorhombic symmetry.

crystals to the tetragonal phase depends on the particular features of the fabrication of the samples.

2. In the entire oxygen concentration range, except at the point $x = 7$, the oxygen in the $YBa_2Cu_3O_x$ crystals is distributed highly nonuniformly when the method of fabrication of the samples described above is used. The diffuse superconducting phase transition occurring when $x < 7$ is evidence in favor of this conclusion.

3. The $T_c(x)$ curve obtained by us has a clearly defined plateau in the concentration region $6.5 \lesssim x \lesssim 6.85$ and at temperatures in the range $T_c = 55$–65 K. The function $T_c(x)$ generally depends on the method of fabrication of the samples (see Ref. 1).

4. The superconducting properties of $YBa_2Cu_3O_x$ single crystals are irregular in nature when $x \lesssim 6.5$ and are highly sensitive to the previous history of the samples. In this range of oxygen concentrations the superconductivity of $YBa_2Cu_3O_x$ could conceivably be "extrinsic" in nature and could occur as a result of a nonuniform distribution of oxygen.

On the basis of the experimental observations, taken collectively, we conclude that the plateau on the $T_c(x)$ curve at ~ 60 K should not be interpreted in the spirit of the existence of a particular phase in the thermodynamic context of this work. The results of x-ray measurements also point to this conclusion.[4] The fact that under certain conditions the function $T_c(x)$ becomes a step function suggests, nonetheless, that a certain ordering, of a "quasimolecular" or cluster type, in the distribution of oxygen atoms occurs in the composition region $6.5 \lesssim x \lesssim 6.85$ (see Refs. 3 and 4).

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