

Evolution of transport properties of ceramic $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ as oxygen is removed by heat treatment

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The change in the temperature dependence of the resistance, $R(T)$, of ceramic $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ as oxygen is removed from the sample has been studied. The superconducting transition temperature shifts progressively downward in the process. There is no significant broadening of the transition. The temperature dependence of the resistivity, $\rho(T)$, is linear, with a progressively increasing slope, only at $T > 400$ K. It is suggested that oxygen condenses on Cu–O chains at $T \approx 400$ K.

From the numerous measurements of the shape of the superconducting transition curves of ceramic $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ as a function of the oxygen content, we can distinguish three basic scenarios. Two of them are described in the review by Green and Bagley.¹ According to the first, a narrow transition at $x \approx 0$, with $T_c \approx 90$ K, initially broadens with increasing x in the temperature interval between 90 K and 60 K. It then contracts at $T_c \approx 60$ K and finally becomes very broad again at $T < 60$ K (Refs. 2 and 3). According to the second scenario, the transition at $x > 0$ is a two-stage process, with $T_{c1} \approx 90$ K and $T_{c2} \approx 60$ K (Ref. 1). According to the third scenario, a transition

is possible at any $T_c \leq 90$ K, and its width depends only slightly on T_c (Refs. 4 and 5).

In an attempt to sort out the reasons for this diversity and to relate the shape of the transitions curves to the transport properties in the normal state, we have undertaken a series of measurements on a single sample. We alternately annealed it at $T \approx 700$ – 800 K and measured its resistance over the temperature range from 700 K to 4 K. We are reporting the preliminary results of these experiments in the present letter.

Test samples and experimental procedure. The test sample, with dimensions of $3 \times 3 \times 10$ mm, with brazed silver contacts, was held in a hermetically sealed cell, which was connected to a buffer chamber with a volume more than four orders of magnitude greater than that of the sample. Because of this disparity in volume, the pressure of the oxygen evolved from the sample was negligible in all stages of the experiment. A small amount of helium was admitted into the cell for heat transfer.

The basic criterion used in the adjustment of the annealing process was the change in the resistance of the sample, R . The annealing, which was carried out at a fixed temperature T_{\max} and which lasted about 1–2 h, was terminated when R increased by about 10–15%. The time taken to raise the temperature from room temperature to T_{\max} and to lower it after the annealing was again about 2 h. A total of about 20 annealing cycles were carried out. In the first few cycles, T_{\max} was about 720 K; it was progressively raised to 800 K in the subsequent cycles. We measured $R(T)$ in each cycle. To monitor the reproducibility, we measured R as the temperature was both lowered and raised.

The resistivity of the original sample at room temperature was $\rho \approx 2 \times 10^{-3}$ $\Omega \cdot \text{cm}$, its density was 5.3 g/cm^3 , and the average grain size was 5 μm .

Experimental results. Some of the $R(T)$ curves recorded are shown in Fig. 1. While the plot of $R(T)$ for the initial state was linear over the wide temperature range down to T_c , a “semiconducting” region quickly appeared on the curves, and the linear high-temperature behavior was cut off fairly sharply at $T \approx 350$ – 400 K (the slope change marked by the arrows).

The $R(T)$ behavior in the temperature range 400 – 600 K has been discussed only on comparatively rare occasions. Most of the research has focused on temperatures below room temperature or on high temperatures, at which the dynamic equilibrium of oxygen is established.^{6,7} Although the range 400 – 600 K is a range of fairly high temperatures, the oxygen concentration in the sample is not yet changing here. We can describe this part of the $R(T)$ curves by

$$R(T) = R_0 + DT, \quad D = dR/dT \Big|_{400\text{K}} \quad (1)$$

(the dashed lines in Fig. 1) and compare the changes in R_0 and D (Fig. 2). Of particular interest is the interval of states with $R_0 = \text{const}$ and increasing D .

Since all the measurements were carried out on a single sample, in comparing the curves we do not have to consider effects of an initial scatter in the properties of the samples or an uncertainty in the positions of the contacts. On the other hand, it may have happened that the removal of oxygen during the annealing was accompanied by

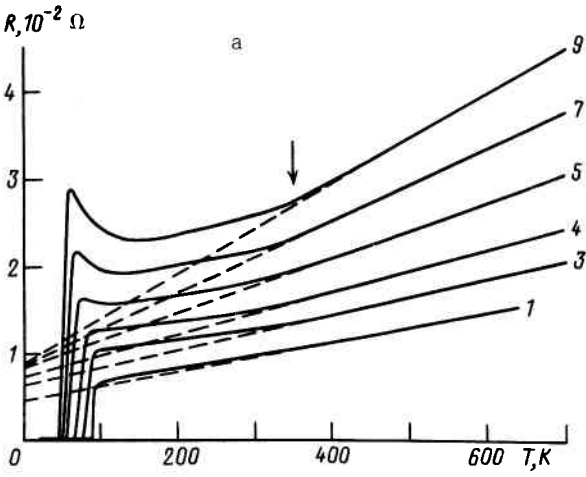
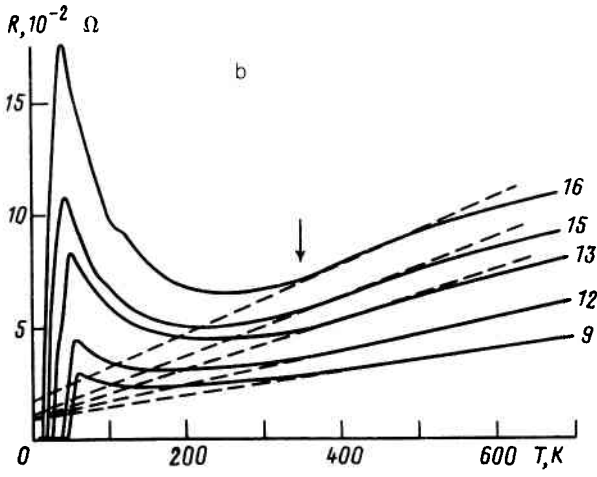


FIG. 1. (a,b). The resistance of the sample, R , versus the temperature T ; the curve label is the order of the annealing cycle.

the development of a spatial irregularity in the sample. Such an event might have changed the shape of current channels in the sample; i.e., it might have altered the geometric factor φ in the relation

$$R = \rho \varphi . \tag{2}$$

Changes in φ at a fixed ρ lead to a proportionality $R \propto D$.

A constant value of R_0 in the face of an increase in D is thus a central experimental fact, which supports the assertion that the factor φ remains constant in the corresponding interval of states; i.e., the removal of oxygen occurs uniformly over the sample. It follows immediately that we have $\rho_0 = \text{const}$ in this interval.

According to the standard description of a metallic state we would have

$$\rho = \rho_0 + \rho_1(T) = (p_F / ne^2)(l_0^{-1} + l_1^{-1})$$

[p_F is the Fermi momentum, and l_0 and $l_1 = l(T)$ are the residual and temperature-dependent parts of the mean free path l_0]. It then follows from the result $r_0 = \text{const}$ that we have either $n = \text{const}$ and $l_0 = \text{const}$ or $l_0 \propto n^{-1}$. In the latter case, the number of scattering centers would be equal to the number of carriers.

A second conclusion which can be drawn from the constant value of φ can be formulated thus: As x is reduced, there is an increase in $d\rho/dT$. This result, combined with the decrease in T_c (Fig. 2), indicates that D is not the measure of the electron-phonon interaction which is responsible for the superconducting transition in the BCS theory.

It can be seen from Fig. 1 that in the final cycles the linear region of the $R(T)$ plot shrinks from the high-temperature side also, where a tendency toward saturation replaces the linear region. This behavior is highly reminiscent of the saturation of the resistance which occurs when the mean free path l reaches its natural limit, the size of the unit cell.⁸ This result may therefore be regarded as one more piece of evidence, although indirect, in favor of a relationship $R(D) \propto \rho(D)$.

Figure 3 shows the progressive shift of the superconducting transition curve. We see that the onset and end of the transition are by no means tied to either 90 K or 60 K and that the width of the transition, which increases after the first few cycles, subsequently remains basically constant [see also the curves of $T_c^{(0)}(D)$ and $T_c^{(j)}(D)$ in Fig. 2]. This is the third of the scenarios outlined above. A splitting of the transition occurs only at $T_c \lesssim 50$ K, but the positions of the steps are apparently not tied to definite temperatures (cf. Ref. 3).

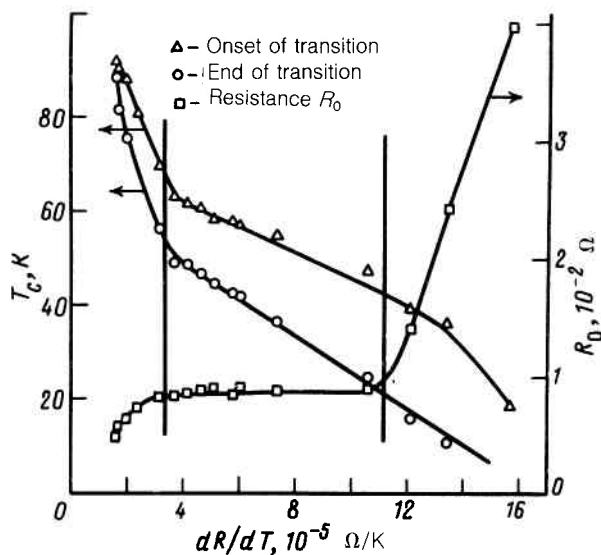


FIG. 2. Superconducting transition temperature and residual resistance R_0 as functions of the slope dR/dT .

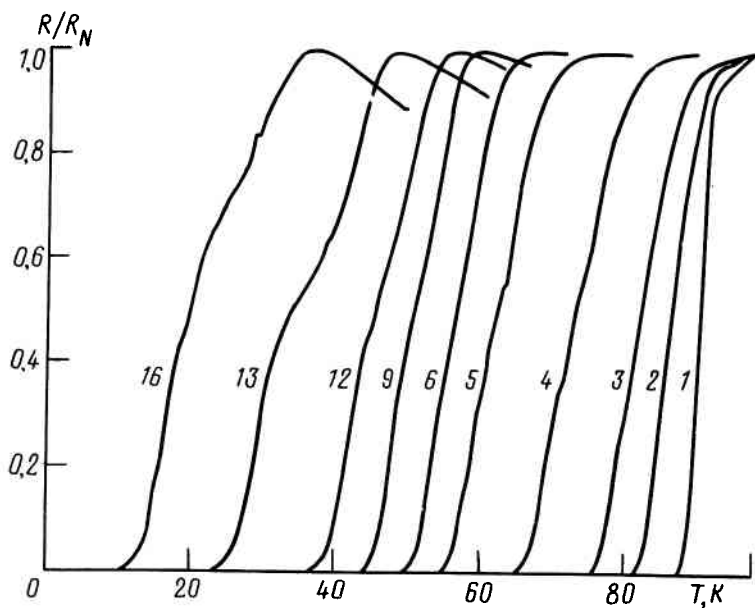


FIG. 3. Curves of $R(T)$ near the superconducting transition, normalized to the resistance in the normal state. The curve label is the order of the annealing cycle.

Discussion. Numerous studies of the positions of the oxygen atoms in Cu-O chains agree that the oxygen in $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ exhibits a tendency toward a condensation, filling neighboring positions in the chains.^{9,10} The 90-K phase (the ortho-I phase) corresponds to $x = 0$ and to a complete filling of all chains, while the 60-K phase (ortho-II) corresponds to $x = 0.5$ and to an alternation of vacant and filled chains.^{4,5} The condensation temperature T_2 is definitely lower than the “tetra-ortho” transition temperature T_1 . According to Ref. 11, we have $T_2 = T_2(x)$, and this temperature varies over the interval 200–600 K. We believe that the slope changes marked by the arrows in Fig. 1 are a manifestation of specifically a condensation process. In our experiments we found $T_2 \approx 350\text{--}400$ K.

Such a low temperature makes it possible to explain the existence of a variety of scenarios for the evolution of the superconducting transition curves. Specifically, in single crystals or large-grain ceramics with a small number of defects, the material breaks up into 90-K and 60-K domains at $0 < x < 0.5$ (Ref. 12), and the transition to a superconducting state becomes a two-step transition.¹ As always, the domains have a certain equilibrium size Q . The existence of this parameter is responsible for a different version of the structure in a fine-grain material. Because of the low temperature T_2 , the oxygen cannot overcome such barriers as grain boundaries during the condensation. If the grain size is smaller than Q , a breakup into domains thus cannot occur, and the ordering is established only at a lower level: The filled and vacant chains alternate more or less regularly, in proportions which depend on x (Refs. 13–15). In such a material, T_c can take on any value between 90 K and 60 K.

Similar structural versions apparently exist at $x > 0.5$ (Refs. 13 and 16), although this question has not received much study.

Conclusion. An experimentally observed version of the evolution of the transport properties and the superconducting transition curves of ceramic $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ as oxygen leaves the sample has been described here. Various versions of the ordering of oxygen have been considered in an effort to explain the existence of a variety of evolution scenarios. It has been suggested that the condensation of oxygen in chains occurs at such a low temperature T_2 that the breakup into domains occurs only in a defect-free material, and only a local ordering occurs in a fine-grained sample.

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