# THE ROLE OF COPPER VALENCIES IN ORTHORHOMBIC $YBa_2Cu_3O_x$ ON THE ELECTRICAL RESISTIVITY

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An investigation of the temperature dependence of the resistivity $\rho(T)$ of the orthorhombic $YBa_2Cu_3O_x$ samples prepared by annealing and quenching was carried out. A distinction in some properties of the samples which possess identical oxygen content but are prepared by these two different methods is clearly demonstrated. An explanation connected with different processes of order–disorder and different amounts of $Cu^{3+}$ states in annealing and quenching specimens is proposed.

**Key words**: oxygen–deficient high temperature superconductors, order–disorder processes, annealing, quenching, resistivity.

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## I. INTRODUCTION

In the past few years oxygen–deficient $YBa_2Cu_3O_x$ samples prepared by various methods have been extensively studied. Now it is well established [1–5] that the oxygen content and the ordering of the oxygen atoms in the crystal lattice strongly influence the physical properties of these compounds.

Many authors claim that for the metastable oxygen–deficient YBCO compounds with the same oxygen contents but prepared in different ways one may expect significant differences in their properties [6–8]. This behaviour has been attributed to the possibility that different sample prehistories lead to the different metastable states for samples with identical oxygen contents. This confirms the conclusion that the spatial arrangement of the oxygen atoms and not only their average concentration determines the properties of these compounds.

All previous studies of the intriguing effects concerning oxygen–deficient $YBa_2Cu_3O_x$ compounds were performed on samples having tetragonal symmetry or on quenched samples after different annealing procedures. There are experiments which compare the physical properties of tetragonal $YBa_2Cu_3O_x$ samples with identical oxygen contents but prepared in different ways. It seems interesting to investigate the same problem for orthorhombic $YBa_2Cu_3O_x$ samples. Obviously, such experiments are difficult due to the problems in stabilizing the total sample volume in a particular ordered state and in comparing such a sample with those with the same oxygen content but without ordering.

Now it is well known that quenching the $YBa_2Cu_3O_x$ samples leads to the freezing of the disordered non–equilibrium state. Conversely, a long annealing at a relatively low temperature is the required to decrease the oxygen vacancies and the randomness of these compounds [6–9].

In this paper experimental results are presented demonstrating important differences in some properties of $YBa_2Cu_3O_x$ orthorhombic samples which possess identical oxygen contents but are prepared by two different methods: a liquid nitrogen quenching from high temperature and a gettered annealing technique. An attempt is made to explain these differences by order–disorder processes and various amounts of $Cu^{3+}$ states in annealing and quenching specimens.

## II. EXPERIMENTAL

Fully oxidized polycrystal orthorhombic $YBa_2Cu_3O_x$ samples were prepared from powders of $Y_2O_3$, $BaCO_3$ and CuO mixed in stoichiometric ratios. The powders were heated at 920°C for 12 h in air and ground in ball mill. This process was repeated. The calcined powder was pressed into pellets and then sintered at 920°C for 18 h in oxygen atmosphere. The furnace was slowly cooled with cooling rate 1°C/min down to 500°C where the samples were kept for another 24 h in oxygen flow. At the end of this step, at a temperature labeled as $T^Q_{500}$, one pallet was quickly taken out of the furnace and quenched into liquid nitrogen. Such a procedure was repeated at temperatures 400°C and 300°C and the samples were labeled $T^Q_{400}$ and $T^Q_{300}$, respectively. For the rest of this first group of specimens the cooling rate remains less than 1°C/min down to room temperature. The latter samples become an output material for the next group of specimens.

$X$–ray diffraction patterns, obtained by the use of $CuK_\alpha$ radiation indicated that the samples prepared in this way were single–phase orthorhombic perovskites. Chemical analysis by iodimetry [10], spectrophotometric method [11], thermogravimetry /TGA/ and Raman spectrometry was done to verify the final oxygen content. The precision of the analytical determinations was in the interval 0.01%–0.04%.

The second group of samples was obtained from the first one after gettered annealing. According to this method unquenched pallets from the first group were sealed in an evacuated quartz tube with a properly weighed thin wolfram sheet and fired at appropriate temperature for about 48 h followed by annealing between 400°C and 500°C for 3 days. By changing the wolfram sheet weight, firing temperature and time of firing we obtain samples with varying oxygen content. Among 50 specimens only 3 had the same oxygen concentration and homogeneity as those quenched at 300°C, 400°C and 500°C. They were labeled conditionally $T^A_{300}$, $T^A_{400}$, $T^A_{500}$, respectively. For these samples the final oxygen content was determined by the use of the analytical methods mentioned above. Our further study was concentrated only on these two groups of specimens $T^Q_{300}$, $T^Q_{400}$, $T^Q_{500}$ and $T^A_{300}$, $T^A_{400}$, $T^A_{500}$. All the pairs with identical number indications have identical oxygen concentration but are prepared in different ways. This offered a possibility to compare some properties of a sample in a particular ordered state $T^A$ with those for the disordered sample $T^Q$.

The temperature dependencies of the electrical resistivity $\rho(T)$ were performed for these two groups of specimens using a standard four probe method. The investigated temperature interval, measured by a platinum thermometer with the accuracy 0.01 K, was 77–400 K.

## III. RESULTS AND DISCUSSION

In Table I are presented results for both the investigated groups of samples (annealed $T^A$ and quenched $T^Q$). From Table I it is evident that in spite of the identical oxygen concentration of the annealed and quenched samples with identical number indication they possess different values of all parameters measured in this investigation.

| | ANNEALED | | | QUENCHED | | |
|---|---|---|---|---|---|---|
| | $T^A_{300}$ | $T^A_{400}$ | $T^A_{500}$ | $T^Q_{300}$ | $T^Q_{400}$ | $T^Q_{500}$ |
| $X$ | 6.91 | 6.82 | 6.77 | 6.91 | 6.82 | 6.77 |
| $T_c$ [K] | 94 | 93.5 | 92.5 | 93.0 | 91.5 | 90.5 |
| $\Delta T_c$ [K] | 0.6 | 0.9 | 1.2 | 1.2 | 1.5 | 1.7 |
| $\rho_N$ [$m\Omega$] | 0.4 | 0.8 | 1.5 | 1.4 | 3.4 | 4 |
| $Cu^{3+}$ [%] | 9.35 | 8.75 | 8.5 | 7.84 | 6.21 | 6.1 |

Table I

The differences with respect to $T_c$ (about 2 K) are the smallest and those with respect to the $Cu^{3+}$ content are the largest. The $Cu^{3+}$ concentration was determined by precise iodometric titration measurements and gave a possibility to estimate the percent of the $Cu^{3+}$ states [10].

Another important difference was observed on the temperature dependencies of the resistivity $\rho(T)$ of the annealed and quenched samples with identical oxygen concentration (Fig. 1). In Fig. 1 resistivity data for annealed $T^A_{500}$ and quenched $T^Q_{500}$ samples with $X = 6.77$ are presented. The difference in the temperature dependence of the resistivity $\rho(T)$ is observed for all the measured samples but the effect is most distinctly demonstrated for the concentration of $X = 6.77$, as shown in Fig. 1. For the remaining pairs of samples the shape of the curves $\rho(T)$ does not change qualitatively and the only effects are in the sharpening of the transition, the changes in the absolute values of the normal resistivity $\rho_N$ and the width of the superconducting transition $\Delta T$. Higher $\rho_N$ and $\Delta T$ values in more disordered quenched samples are attributed to a change in oxygen vacancy ordering in the Cu–O chains without a stoichiometry change. A higher $\rho_N$ indicates also a decrease in the charge carrier density in the CuO–planes induced by oxygen disorder. This fact explains also the lower values of $T_c$ for quenched samples.

However, the main distinction between the $\rho(T)$ curves for annealed and quenched specimens was observed above 300 K. At higher temperatures the resistivity of quenched samples increases more rapidly than it could be expected owing to the low temperature dependence. As evident from Fig. 1, such a behaviour of annealed YBCO specimen (○) is not present. A possible explanation of this feature is connected again with the presence of more disordered states in the quenched samples in contrast to the annealed ones where the oxygen subsystem is ordered and induces higher density of charge carriers in the $CuO_2$ planes.

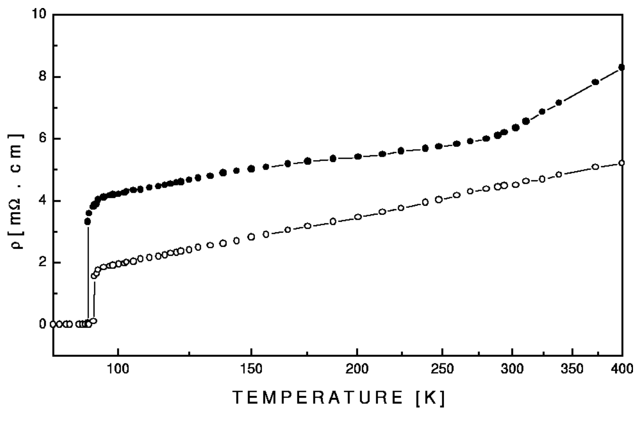


Fig. 1. Temperature dependencies of the resistivity of the annealed (○) and quenched (●) samples.

Another probable explanation is consistent with our $Cu^{3+}$ results presented in Table I. As is known, when equilibrated at high temperature and quenched to low temperature, oxygen can be reversibly removed from the structure depending on the equilibrium temperature. Neutron spectroscopy has been used to show [12] that mainly the $O(1)$ oxygen sites are emptied in this procedure, with the conclusion that the Cu(1) ions are reduced from $Cu^{3+}$ states to $Cu^{2+}$ ones. Some disorder of these oxygen ions of the basal $CuO_x$ plane is retained. On the order hand, for the quenched samples, the presence of O(4) vacancies whose concentration increases with decreasing $x$ has been shown by neutron diffraction [1]. These $O(4)$ vacancies also contribute to the randomness in the quenched specimens and to the reduction from $Cu^{3+}$ to $Cu^{2+}$. As indicated by our $Cu^{3+}$ data (see Table I), the samples with the lower quenching temperature $T_{300}^{Q}$ have a higher percentage of $Cu^{3+}$ states. However, the values of the $Cu^{3+}$ concentrations in Table I are lower than the $Cu^{3+}$ concentration values of all annealed samples. We presume that the order–disorder processes in the oxygen subsystem are not the only effects responsible for the observed additional change of the resistivity. The process of reduction from $Cu^{3+}$ into $Cu^{2+}$ states and the availability of $O(4)$ vacancies in the quenched samples seem to give reliable explanation of this interesting temperature dependence on resistivity.

## IV. CONCLUSION

A study of the temperature dependence of the electrical resistivity $\rho(T)$ for two groups of samples prepared by annealing and quenching has been conducted. It has been definitely demonstrated that the specimens with identical oxygen concentration but having different preparation techniques, exhibit differences in all the measured parameters. The main distinction in the $\rho(T)$ curves for annealed and quenched samples is in the additional change of resistivity for the quenched ones above 300 K. A probable explanation of this feature is connected with different process of order–disorder and different amounts of $Cu^{3+}$ states in annealed and quenched specimens. It is most likely that both processes take place in the mechanism of this additional change of the resistivity in the quenched samples. This work shows that for oxygen–deficient orthorhombic $YBa_2Cu_3O_x$ not only the oxygen concentration but also the degree of ordering and amounts of $Cu^{3+}$ states are responsible for its physical properties.

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