Electrical conductivity of YBa$_2$Cu$_3$O$_{7-\delta}$ single crystals under conditions of anionic ordering in Cu(1)O$_{1-\delta}$ layers

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Received 11 March 2020 ♦ Accepted 3 April 2020 ♦ Published 30 June 2020

Citation: Kalanda NA (2020) Electrical conductivity of YBa$_2$Cu$_3$O$_{7-\delta}$ single crystals under conditions of anionic ordering in Cu(1)O$_{1-\delta}$ layers. Modern Electronic Materials 6(2): 53–57. https://doi.org/10.3897/j.moem.6.2.58097

Abstract

The influence of thermocycling annealing processes on the oxygen ordering degree (order parameter) in YBa$_2$Cu$_3$O$_{7-\delta}$ single crystals has been studied. It has been shown that an increase in the critical onset temperature of the transition to the superconducting state during thermocycling annealing procedures is consistent with the decrease of the $\sigma_c/\sigma_{ab}$ parameter. This fact indicates a redistribution of the electronic density between the structurally inhomogeneous Cu(2)O$_2$ and Cu(1)O$_{1-\delta}$ planes, due to the formation of oxygen long-range order in the O(4)–Cu(1)–O(4) linear groups along the (b) crystal structure axis of the unit cell, and elimination of oxygen defects in the square nets of the Cu(2)O$_2$ planes. The existence of the critical value of the conductivity anisotropy $\sigma_c/\sigma_{ab}$ below which its behavior does not correlate with the change of $T_c$, has been confirmed. In this case an increase in $T_c$ and orthorhombic distortion of the crystal structure during isothermal annealing are caused by the amplification of the “interlayer” interaction between the Cu(2)O$_2$ and Cu(1)O$_{1-\delta}$ planes. As a result, the contribution of the Cu(1)O$_{1-\delta}$ chain layers to the electron state density at the Fermi level increases. These layers can acquire superconducting properties due to tunneling of Cooper pairs from the Cu(2)O$_2$ planes resulting in the formation of the induced superconductivity in these planes.

Keywords

high-temperature superconductivity, YBa$_2$Cu$_3$O$_{7-\delta}$ single crystals, oxygen non-stoichiometry, electrical conductivity, order parameter.

1. Introduction

An urgent task in the research of high-temperature superconductivity is to improve the technology of high-quality specimens including the YBa$_2$Cu$_3$O$_{7-\delta}$ compound having reproducible superconducting properties and to study their physico-chemical properties. One condition of the existence of the superconducting state in cuprate compounds is that planes perpendicular to the crystallographic $C_4$ axis and those parallel to that axis should contain virtually square nets with minor rhombic distortion. The sites of the squares should be occupied by O$^2$ oxygen anions and their centers should accommodate variable valence copper cations, i.e., Cu$^{1+}$-$^{2+}$-$^{3+}$, the average valence evaluated from the length of the Cu–O bond being ~2.33 [1, 2]. Analysis of the dependence of the superconducting properties of YBa$_2$Cu$_3$O$_{7-\delta}$ on oxygen non-stoichiometry has shown that the critical temperature of the onset of the transition to the superconducting state ($T_c$) is controlled by the density of electronic states $N(E_F)$ at the Fermi level $E_F$ which are in turn associated with the concentration of oxygen vacancies (δ) and their distribution in the YBa$_2$Cu$_3$O$_{7-\delta}$ structure [3–7]. $T_c$ is known to depend on the concentration of mobile oxygen distributed in the chain Cu(1)O$_{1-\delta}$ planes and may...
reach the highest level (~92 K) at \( \delta = 0\pm 0.2 \) [8]. This correlation is however not definitive since \( T_c \) may vary at a constant \( \delta \) due to the effect of not only the concentration of oxygen vacancies but also their ordering in the anionic sublattice of \( \text{YBa}_2\text{Cu}_3\text{O}_{7-\delta} \) crystals [9–14]. The order parameter of oxygen vacancies (\( \eta_v \)) is in turn controlled by temperature and annealing time and therefore affects \( T_c \) [15–18]. Thus ordering of oxygen vacancies in \( \text{YBa}_2\text{Cu}_3\text{O}_{7-\delta} \) can be considered as one method to change the carrier concentration in the square nets of the Cu(2)O structural planes which determine the superconducting properties of the compound [19–22].

Despite the large number of works on the topic, the ordering conditions of oxygen vacancies between the (0 1/2 0) and (1/2 0 0) structural planes in the \( \text{YBa}_2\text{Cu}_3\text{O}_{7-\delta} \) anionic sublattice, especially at \( \delta \rightarrow 0 \), have been studied insufficiently yet. It is therefore an important task to evaluate the threshold temperature (\( T_{\text{thr}} \)) at which the energy of the thermal atomic oscillations becomes higher than the oxygen bond energy in the \( \text{Cu(1)–O(4)–Cu(1)–O(4)} \) chains and starts to violate the order of oxygen vacancies in the anionic sublattice.

### 3. Results and discussion

The highest diamagnetic response was observed in the crystal after the fourth annealing stage. In that crystal the diamagnetic response was 3.7 times higher than after single-stage annealing. Therefore the superconducting transition temperature increases and the transition width decreases as indicated by the single crystal magnetization temperature functions (Fig. 1). Further increase of the number of annealing stages did not improve the superconducting parameters of the crystals.

![Figure 1. YBa\textsubscript{2}Cu\textsubscript{3}O\textsubscript{7-\delta} single crystal magnetization as a function of temperature after thermocycling annealing: a, b, c and d after the first, second, third and fourth annealing stages, respectively. Inset shows crystal surface image in polarized light.](image)

These results combined with data on field functions of magnetization allowed evaluating the critical current of the crystal using the Bean model:

\[
J_c = 20|\mathbf{M}^+ - \mathbf{M}/|h, \tag{1}
\]

where \( \mathbf{M}^+ \) and \( \mathbf{M}^- \) are the magnetizations of the crystal for opposite magnetic induction vectors of the outer magnetic field. Analysis of the field functions of magnetization showed that the plateaus on the hysteresis loops are almost symmetrical (Fig. 2). It is therefore sufficient to substitute \( |\mathbf{M}^+ - \mathbf{M}^-| \) in Eq. (1) for the double residual moment of magnetization \( M_{\text{res}} \) which equals to the crystal magnetization in a zero field after application of a strong magnetic field (14 T). Then the equation of the critical current density in the crystal takes on as follows:

\[
J_c \approx 40 M_{\text{res}}/h, \tag{2}
\]

The magnetization curves \( M(B) \) at \( T = 7 \) K in magnetic field \( B \) parallel to the \( c \) axis show that with an increase in the number of annealing stages, the areas of the hysteresis loops and hence \( M_{\text{res}} \) increase significantly (Fig. 2).
In accordance with Eq. (2) the annealing process described above increases the critical current density \( J_c \approx 0.68; 1.21; 2.05; 2.59 \times 10^{4} \text{ A/cm}^2 \) for the first, second, third and fourth annealing stages, respectively.

The effect of gas thermal annealing of the YBa\(_{2}\)Cu\(_{3}\)O\(_{7-\delta}\) crystal on the concentration and ordering of oxygen vacancies in the (ab) plane between different crystallographic positions (0 1/2 0) and (1/2 0 0) was determined by measuring the electrical conductivity in different crystal directions: along the (c) axis and in a direction parallel to the (ab) plane. This study showed that thermocycling annealing of the crystals caused correlated changes in \( \Delta_{\text{ab}} \) and \( \sigma_{\text{ab}}/\sigma_{\text{c}} \) (Fig. 3). The decrease in the \( \sigma_{\text{ab}}/\sigma_{\text{c}} \) ratio due to a faster increase in \( \sigma_{\text{ab}} \) than in \( \sigma_{\text{c}} \) is caused by different mechanisms of the effect of thermocycling annealing on the electrical conductivity of the crystal in different directions.

One can assume that the growth of \( \sigma_{\text{c}} \) is caused by an increase in the degree of covalence of the bond along the c axis of the YBa\(_{2}\)Cu\(_{3}\)O\(_{7-\delta}\) lattice leading to an increase in the overlapping of the wave functions of electrons located on the Cu3d\(_{z}\) orbitals of copper and the O2p\(_{z}\) orbitals of oxygen. This assumption is confirmed by a decrease in the lattice parameter along the (c) axis (Table 1).

The increase in the electrical conductivity \( \sigma_{\text{ab}} \) after thermocycling annealing is caused by a redistribution of the electronic density from the square nets of the Cu(2)O\(_{2}\) layers to the Cu(1)O\(_{3}\) chain layers which leads to an increase in \( N(E)_{\text{p}} \) in Cu(2)O\(_{3}\). The redistribution of the electronic density is affected by the concentration and ordering of oxygen vacancies along (a) or an increase in the occupation density of (0 1/2 0) crystallographic positions by oxygen anions leading to an increase in the orthorhombic distortion \( \Delta_{\text{ab}}' \).

After constant \( T_c \) and \( \sigma_{\text{c}}/\sigma_{\text{ab}} \) were achieved we started isothermal annealing in the 720–560 K range at \( pO_2 = 5 \times 10^{5} \text{ Pa} \) for 15 h. \( T_c \) increased at \( \Delta T_c = \text{const} \) at temperatures below the threshold one \( T_c = 600 \text{ K} \) (Fig. 4). Furthermore \( \sigma_{\text{c}}/\sigma_{\text{ab}} \) remained constant during isothermal annealing in the 660–560 K range whereas \( T_c \) increased. The increase in \( T_c \) can be arbitrarily split in two regions I and II with \( T_c \) increasing faster in the region I than in the region II (Fig. 4).

For determining \( T_c \) as a function of oxygen vacancy concentration and ordering, the order parameter was introduced which depends linearly on the orthorhombic distortion \( \Delta_{\text{ab}}' \) and is expressed analytically as \( \Delta_{\text{ab}}' = \alpha n v \), where \( \alpha \) is the proportion coefficient. This latter proportion

<table>
<thead>
<tr>
<th>( n )</th>
<th>( T_c, \text{K} )</th>
<th>( \Delta T_c, \text{K} )</th>
<th>( \Delta_{\text{ab}}', \text{nm} )</th>
<th>( n_0, \text{nm} )</th>
<th>( \eta_0 )</th>
<th>( \delta )</th>
</tr>
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<td>1</td>
<td>84.2</td>
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<td>1.17085</td>
<td>0.3333</td>
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<tr>
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<td>2</td>
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<tr>
<td>3</td>
<td>88.5</td>
<td>1.5</td>
<td>0.00597</td>
<td>1.17101</td>
<td>0.3826</td>
<td>0.11</td>
</tr>
<tr>
<td>4</td>
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<td>1</td>
<td>0.00606</td>
<td>1.17001</td>
<td>0.3884</td>
<td>0.10</td>
</tr>
</tbody>
</table>

Figure 2. Field dependences of the magnetization of the YBa\(_{2}\)Cu\(_{3}\)O\(_{7-\delta}\) single crystal; a, b, c and d after the first, second, third and fourth annealing stages, respectively.

Figure 3. Influence of the number of thermocycling annealing processes on the anisotropy of conductivity and the onset temperature of the YBa\(_{2}\)Cu\(_{3}\)O\(_{7-\delta}\) crystal transition to the superconducting state.

Figure 4. Kinetic dependence of the superconducting transition onset temperature (\( T_c \), K) for the YBa\(_{2}\)Cu\(_{3}\)O\(_{7-\delta}\) crystals annealed at \( pO_2 = 5 \times 10^{5} \text{ Pa} \) and at various temperatures under isothermal conditions.

Table 1. Dependence of the superconducting characteristics and crystal lattice parameters of the YBa\(_{2}\)Cu\(_{3}\)O\(_{7-\delta}\) single crystal on the number of thermocycling annealing stages (\( n \)).
coefficient is calculated for the maximum value max(Δ_{b-a}) = 0.00780 nm for the stoichiometric composition of YBa₂Cu₃O_7-δ, corresponding to δ = 0.5 [28]. The T_c parameters of the thermocycled crystals are more sensitive to the concentration of oxygen vacancies (δ) than to their ordering (η_{v'}). (Tables 1, 2). During isothermal annealing in the 660–560 K range the ordering of oxygen vacancies makes the largest contribution to the changes in T_c. Then only η_{v'} change whereas δ = const. An increase in η_{v'} is caused by the ordering of oxygen anions accompanied by an increase in the length of the −Cu(1)−O(4)−Cu(1)−O(4)− chain fragments. This is auspicious for an increase in the covalence degree of the bonds along the structural direction a, a decrease in the length of the −Cu(1)−O(1)−Cu(2)− bond with a redistribution of the electronic density from the square nets of the Cu(2)O planes to the Cu(1)O planes, and an increase in the free carrier concentration at the antibonding Cu3d_{(x2-y2)}-O2p_y hybridized orbitals. The difference in the T_c growth rates between the regions I and II stems from the fact that oxygen ordering in the −Cu(1)−O(4)−Cu(1)−O(4)− chains along the (b) axis (region I) requires atomic movements through an order of one interatomic distance whereas for the region II long chain ordering along the (b) axis requires anion movements through quite large distances.

<table>
<thead>
<tr>
<th>Isothermal Annealing (T, K)</th>
<th>T_{c} , K</th>
<th>ΔT, K</th>
<th>Δ_{c-b} nm</th>
<th>(b) nm</th>
<th>η_{v'}</th>
<th>δ</th>
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<tbody>
<tr>
<td>660</td>
<td>91.7</td>
<td>1</td>
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<td>1.16900</td>
<td>0.4429</td>
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<td>580</td>
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<td>0.4378</td>
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</table>

4. Conclusion

Study of the regularities of oxygen interaction with yttrium/barium cuprate single crystals for the first time justified the necessity of using multistage gas thermal treatment in order to increase the superconducting parameters of YBa₂Cu₃O_7-δ due to intentional impact on oxygen sorption and ordering processes in its anionic sublattice. An increase in the critical onset temperature of the transition to the superconducting state during this annealing is consistent with the decrease of the σ/σ_0 parameter. This fact indicates a redistribution of the electronic density between the structurally inhomogeneous Cu(2)O planes and Cu(1)O planes, due to the formation of oxygen long-range order in the O(4)-Cu(1)-O(4) linear groups along the (b) crystal structure axis of the unit cell, and elimination of oxygen defects in the square nets of the Cu(2)O planes.

The existence of the critical value of the conductivity anisotropy σ/σ_0, below which its behavior does not correlate with the change of T_c, was confirmed. In this case an increase in T_c and orthorhombic distortion of the crystal structure during isothermal annealing are caused by the amplification of the “interlayer” interaction between the Cu(2)O planes and Cu(1)O planes. As a result, the contribution of the Cu(1)O planes to the density of electronic state at the Fermi level increases. These layers can acquire superconducting properties due to tunneling of Cooper pairs from the Cu(2)O planes resulting in the formation of the induced superconductivity in these planes.

Acknowledgments

This work was carried out in frames of the European Uni-

on Project H2020-MSCA-RISE-2017-778308 – SPIN-

MULTIFILM and Task No. 1.02 of the State Program of

Scientific Research of the Republic of Belarus “Physical

Materials Science, New Materials and Technologies”, Sub-

program “Materials Science and Materials Technologies”.

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