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

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Abstract

The influence of thermocycling annealing processes on the oxygen ordering degree (order parameter) in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ 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 $\text{Cu}(2)\text{O}_2$ and $\text{Cu}(1)\text{O}_{1-\delta}$ 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 $\text{Cu}(2)\text{O}_2$ 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 $\text{Cu}(2)\text{O}_2$ and $\text{Cu}(1)\text{O}_{1-\delta}$ planes. As a result, the contribution of the $\text{Cu}(1)\text{O}_{1-\delta}$ 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 $\text{Cu}(2)\text{O}_2$ planes resulting in the formation of the induced superconductivity in these planes.

Keywords

high-temperature superconductivity, $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ 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 $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ 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 $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ 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 ($\delta$) and their distribution in the $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ structure [3–7]. $T_c$ is known to depend on the concentration of mobile oxygen distributed in the chain $\text{Cu}(1)\text{O}_{1-\delta}$ planes and may...
reach the highest level (−92 K) at $\delta = 0.2$ [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 YBa$_2$Cu$_3$O$_{7-\delta}$ crystals [9–14]. The order parameter of oxygen vacancies ($n_\delta$) is in turn controlled by temperature and annealing time and therefore affects $T_c$ [15–18]. Thus ordering of oxygen vacancies in YBa$_2$Cu$_3$O$_{7-\delta}$ can be considered as one method to change the carrier concentration in the square nets of the Cu(2)O$_2$ 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 YBa$_2$Cu$_3$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 ($T_{th}$, K) at which the energy of the thermal atomic oscillations becomes higher than the oxygen bond energy in the –Cu(1)–O(4)–Cu(1)–O(4)– chains and starts to violate the order of oxygen vacancies in the anionic sublattice.

2. Experimental

The YBa$_2$Cu$_3$O$_{7-\delta}$ single crystals were zone melt grown with directional mass transport in the system of [Ba$_2$Cu$_3$O$_{5}$ + xBaCuO$_2$]/YBaCuO$_3$ diffusion pairs due to the component concentration gradient between the contacting layers [23, 24]. The Y$_2$BaCuO$_5$ and BaCuO$_2$ compounds were synthesized using high purity grade Y$_2$O$_3$, BaO and CuO oxides. The compounds were synthesized in thermal plants at 1220 K, 1270 K and $p_{O_2} = 0.21 \times 10^5$ Pa for BaCuO$_2$ and Y$_2$BaCuO$_5$, respectively. The temperature in the thermal plants was maintained using a RIF-101 high-precision temperature controller and was monitored with a Pt-Pt/Rh(10%) thermocouple accurate to ± 0.5 K. The as-grown single crystals had sizes of $1 \times 1 \times 0.5 \div 5 \times 4 \times 2 \ mm^3$, $\delta = 0.6–0.7$ and the superconducting parameters $T_c = 31–36 \ K$ and $\Delta T_c = 11–18 \ K$, where $\Delta T_c = 90–10 \%$ is the width of the temperature transition to the superconducting state. The structure of the single crystals was studied on a DRON-3 diffractometer in CuK$_\alpha$ radiation. The lattice parameters were determined using the asymmetrical method accurate to $\pm 5 \times 10^{-5}$ nm for YBa$_2$Cu$_3$O$_{7-\delta}$ powders.

Since the saturation rate and subsequent oxygen ordering in YBa$_2$Cu$_3$O$_{7-\delta}$ triple cuprate are far lower for single crystals and dense ceramics ($\rho = 6.0–6.2 \ g/cm^3$) than for moderate density ceramic specimens ($\rho = 4.4–4.7 \ g/cm^3$), the parameter value $\delta \leq 0.1$ was achieved using three stage thermocycling annealing [25–27]. At the initial stage the YBa$_2$Cu$_3$O$_{7-\delta}$ crystals were annealed at 820 K for 2 h and at the second stage, at $T = 1020 \ K$ for 2 h and at the third stage they were stepwise cooled at a 40–50 K/h rate within the 1020–870 K range and at a 1–5 K/h rate in the 870–720 K range. The electrical conductivity of the YBa$_2$Cu$_3$O$_{7-\delta}$ crystals was measured in the 77–800 K range using the four-probe method with platinum contacts.

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](image)

Figure 1. YBa$_2$Cu$_3$O$_{7-\delta}$ 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.

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

$$J_c = 20|–M^* + M|/h,$$  (1)

where $M^*$ and $M^*$ 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 $|–M^* + M|$ in Eq. (1) for the double residual moment of magnetization $M_{res}$ 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:

$$J_c \approx 40 \ M_{res}/h,$$  (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 $M_{res}$ 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\(_{\delta}\) 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 \( \sigma_{\text{ab}} \) and \( \sigma_{\text{c}} / \sigma_{\text{ab}} \) (Fig. 3). The decrease in the \( \sigma_{\text{c}} / \sigma_{\text{ab}} \) ratio due to a faster increase in \( \sigma_{\text{c}} \), than in \( \sigma_{\text{ab}} \), is caused by different mechanisms of the effect of thermocycling annealing on the electrical conductivity of the crystal in different directions.

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\(_2\) chain layers which leads to an increase in \( N(E)_0 \) in Cu(2)O. 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 \( T_p \) and \( \sigma / \sigma_{\text{ab}} \) were achieved we started isothermal annealing in the 720–560 K range at \( p_{\text{O}_2} = 5 \times 10^9 \text{Pa} \) 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 \( \sigma / \sigma_{\text{ab}} \) 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 \( \Delta_{\text{ab}} = \alpha n_{\text{O}_2} \) where \( \alpha \) is the proportion coefficient. This latter proportion

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### Table 1. Dependence of the superconducting characteristics and crystal lattice parameters of the YBa\(_2\)Cu\(_3\)O\(_{\delta}\) single crystal on the number of thermocycling annealing stages (n).

| n | \( T_c \), K | \( \Delta T_c \), K | \( \Delta_{\text{ab}} \), nm | (a), nm | \( p_{\text{O}_2} \), atm | \( \Delta_{\text{ab}} \) |
|---|---|---|---|---|---|---|
| 1 | 84.2 | 4 | 0.0052 | 1.17085 | 0.3333 | 0.15 |
| 2 | 87.1 | 2 | 0.00572 | 1.17034 | 0.3666 | 0.13 |
| 3 | 88.5 | 1.5 | 0.00597 | 1.17010 | 0.3826 | 0.11 |
| 4 | 89 | 1 | 0.00606 | 1.17001 | 0.3884 | 0.10 |

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**Figure 2.** Field dependences of the magnetization of the YBa\(_2\)Cu\(_3\)O\(_{\delta}\) 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\(_{\delta}\) 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\(_{\delta}\) crystals annealed at \( p_{\text{O}_2} = 5 \times 10^9 \text{Pa} \) and at various temperatures under isothermal conditions.
coefficient is calculated for the maximum value \(\max(\Delta_{ab}) = 0.00780 \text{ nm}\) for the stoichiometric composition \(\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}\) corresponding to \(\eta_{\text{mm}} = 0.5\) [28]. The \(T_e\) parameters of the thermocycled crystals are more sensitive to the concentration of oxygen vacancies (\(\delta\)) than to their ordering (\(\eta_{\text{c}}\)) (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 \(T_e\). Then only \(\eta_{\text{c}}\) change whereas \(\delta = \text{const}\). An increase in \(\eta_{\text{c}}\) is caused by the ordering of anion vacancies 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 \(c\), 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 \(\text{Cu}3d_{(3z^2-r^2)}^-\text{O}2p^-\) hybridized orbitals. The difference in the \(T_e\) 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 2. Dependence of the superconducting characteristics and crystal lattice parameters of the \(\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}\) single crystal on the temperature of isothermal annealing.

| Isothermal Annealing \(T_a\) (K) | \(T_e\) \(\Delta T_e\) (K) | \(\Delta_{ab}\) (nm) | \(\eta_{\text{c}}\) | \(\delta\) |
|-------------------------------|-----------------|-----------------|---------------|--------|
| 660                          | 91.7            | 0.0691          | 1.9690        | 0.4429 |
| 620                          | 92.4            | 0.0750          | 1.1693        | 0.4378 |
| 580                          | 90.7            | 0.0833          | 1.1693        | 0.4378 |

Analysis of the change in the anisotropy of the electrical conductivity after thermocycling and isothermal annealing showed that the increase in \(T_e\) does not necessarily correlate with the changes in \(\sigma_{ab}/\sigma_{c}\). On the one hand the increase in \(T_e\) for the heat treated specimens can be accounted for by an increase in the free carrier concentration in the Cu(2)O planes and an increase in the strength of the interlayer interaction (\(\sigma_{ab}/\sigma_{c}\)) between the Cu(2)O and Cu(1)O planes. On the other hand annealing at 660–560 K and \(pO_2 = 5 \times 10^5\) Pa increases \(T_e\) of the crystals without changing their \(\sigma_{ab}/\sigma_{c}\). This suggests that the anisotropy of the electrical conductivity of the \(\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}\) single crystals depends on the oxygen non-stoichiometry parameter \(\delta\) and is not determined by \(\eta_{\text{c}}\). It is safe to assume that annealing at 660–560 K and \(pO_2 = 5 \times 10^5\) Pa changes the mechanism that controls the superconducting properties of the crystals. Then the increases in \(\sigma_{ab}\) and \(T_e\) originate from the ordering of oxygen ions and are caused by the contribution of the Cu(1)O planes to the electronic density of states at the Fermi level. The Cu(1)O planes can be superconducting due to the proximity effects, and this fact makes possible the existence of induced superconductivity in these layers due to tunneling of Cooper pairs from the Cu(2)O planes.

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 \(\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}\) 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 \(\sigma_{ab}/\sigma_{c}\) parameter. This fact indicates a redistribution of the electronic density between the structurally inhomogeneous Cu(2)O 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 \(\sigma_{ab}/\sigma_{c}\) below which its behavior does not correlate with the change of \(T_e\), was confirmed. In this case an increase in \(T_e\) and orthorhombic distortion of the crystal structure during isothermal annealing are caused by the amplification of the “interlayer” interaction between the Cu(2)O 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.

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References

1. High-temperature superconductivity: fundamental and applied research: collection of scientific articles. Ed. by A.A. Kiselev. Minsk: Mashinostroenie, 1990: 684 p. (In Russ.)
2. Crabtree G.W., Nelson D.R. Vortex physics in high-temperature superconductors. Physics Today. 1997; 50(4): 38–45. https://doi.org/10.1063/1.881715
3. Sreedhar K., Ganguly P. Evolution and the concomitant disappearance of high-\(T_c\) superconductivity with carrier concentration in the \(\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}\) system (0.0<\(\delta<0.9\)): Crossover from a Mott insulator
to a band metal. Phys. Rev. B. 1990; 41(1): 371–382. https://doi.org/10.1103/PhysRevB.41.371

4. Krasin’kova M.V., Fetisov V.B., Potiev A.A. Study of the oxidation process of YBaCuO$_3$-ceramics. Sverkhprovodimost’; fizika, khimiya, tekhnika. 1990; 11: 2627–2633. (In Russ.)

6. Cava R.J., Batlogg B., Krajewski J.J., Rupp L.W., Schneemeyer L.F., Gorling P.K., Glarum S.H., Marshall J.H., Farrow R.C., Waszczak J.V., Hull R., Trevor P. Superconductivity near 70 K in a new family of layered copper oxides. Nature. 1988; 336(6196): 211–214. https://doi.org/10.1038/336211a0

7. Silver T., Pan A.V., Juncos M., Qin M.J., Dou S.X. Developments in high temperature superconductivity. Ann. Rep. Prog. Chem. Cect. C. 2002; 98: 323–373. https://doi.org/10.1039/B1111186H

10. Gibson G., Cohen L.F., Humphreys R.G., MacManus-Driscoll J.L. The order parameter of oxygen atoms and the superconductivity of oxygen underdoped YBa$_2$Cu$_{1-x}$O$_{7-\delta}$ single crystals. Physica B: Condens. Matter., 2014; 436(1): 88–90. https://doi.org/10.1016/j.physb.2013.11.056

11. Marushkin K.N., Nipan G.D., Gavrichkov S.S. The polymorphism of YBa$_2$Cu$_3$O$_{7+\delta}$ single crystals. Crystallization features of YBa$_2$Cu$_3$O$_{7+\delta}$ ceramics. J. Supercond. 1993; 6(5): 313–316. https://doi.org/10.1023/A:1014069228288

12. Sudareva S.V., Kuznetsova E.I., Krinitsina T.P., Bobylev I.B., Romashov E.P. Crystallization features of YBa$_2$Cu$_3$O$_{7+\delta}$ ceramics. J. Supercond. 1993; 6(5): 313–316. https://doi.org/10.1023/A:1014069228288

13. Klimov A.G., Lebedev A.A. Nanostructural inhomogeneity of YBa$_2$Cu$_3$O$_{7+\delta}$ compounds. Physica C: Supercond. 2000; 331(3–4): 263–273. https://doi.org/10.1016/S0921-4534(00)00007-1

14. Gufan A.A., Prus Yu.V. On the origin of orthorhombic deformations in YBa$_2$Cu$_3$O$_{7+\delta}$. Phys. Solid State. 2000; 42(7): 1211–1214. https://doi.org/10.1134/1.1131364

15. Aliaga A.A., Barilo S.N., Kaldana N.A., Katsko A.A. Influence of oxygen stoichiometry on the structure YBa$_2$Cu$_3$O$_{7+\delta}$. Physica C: 1992; 190: 234–241. https://doi.org/10.1016/0921-4534(92)90601-8

16. Vovk R.V., Khadzhii G.Ya., Goulatis I.L., Chronoas A. Fluctuation conductivity of oxygen underdoped YBa$_2$Cu$_{1-x}$O$_{7-\delta}$ single crystals. Modern Electronic Materials. 2020; 6(2): 53–57. https://doi.org/10.1103/RevModPhys.74.485

17. Vovk R.V., Obolenskii M.A., Zavgorodniy A.A., Bondarenko A.V., Goulatis I.L., Siewert A.V. Influence of high pressure on the electrical transport properties of YBa$_2$Cu$_{1-x}$O$_{7-\delta}$. Phys. Solid State. 1990; 32(1): 318–321. (In Russ.)