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On the room-temperature aging effects in $YBa_2Cu_3O_{6+\delta}$

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ABSTRACT

The aging effects in $YBa_2Cu_3O_{6+\delta}$ have been investigated on the low-speed quenched samples in contrast to other similar studies where the high-speed quenched samples were examined. In the framework of the investigation, XPS analysis has been conducted for the samples stored after quenching for the specified times τ and a detailed experimental dependence of the $YBa_2Cu_3O_{6+\delta}$ lattice parameters a, b, and c on both δ and τ has been obtained. The regime of low-speed quenching results in a threefold increase in the aging effect magnitude. Particular cases of the $c(\delta; \tau)$ dependence are well described by a second-order polynomial with applying different coefficients for different τ. The behavior c has been explained on the basis of a simple model of the Coulomb interaction between the CuO_2 and CuO_δ structural planes, in which the hole charge transfer from CuO_δ to CuO_2 takes place providing the standard level of T_c in $YBa_2Cu_3O_{6+\delta}$ (this level is characterized by a maximum T_c of 93 K at $\delta = 0.9$). It has been demonstrated that the $c(\delta; \tau)$ dependence is a good alternative to assessing the hole concentration in $YBa_2Cu_3O_{6+\delta}$. By analyzing the $c(\delta; \tau)$ experimental dependence as well as the data on the hole localization in the pairs Cu—O obtained by XPS, the authors have made a conclusion about the nature of observed aging effects. The latter are likely to be related to the transition of the Cu $3d^9L^{-1}$ electron configuration to Cu $3d^8$ for copper in the basal plane of $YBa_2Cu_3O_{6+\delta}$ at RT.

1. Introduction

It is well known that the superconducting transition temperature T_c of $YBa_2Cu_3O_{6+\delta}$ depends significantly on the oxygen parameter δ, varying from 0 K (at $\delta \approx 0$) to 93 K (at $\delta \approx 0.9$). At a constant δ the temperature T_c is believed to be quite stable and its small changes occurring over time are associated with the processes of chemical degradation [1,2].

It has been established, however, that the $YBa_2Cu_3O_{6+\delta}$ samples ($\delta < 0.7$) just quenched after high-temperature oxidation to room temperature (RT) have the lattice parameters and T_c considerably different from the values found for samples stored for a long time τ (hereafter post-quench time or τ) [3–9]. Eventually, these values reach the level specific for given δ. To illustrate that, let us consider results presented by some groups of investigators. So, in the study of Jorgensen et al. [6], the continuous growth of T_c from 0 to 20 K and the fall of the parameter c were detected for a few days after the $YBa_2Cu_3O_{6.41}$ had been quenched. The authors found these changes to occur by rapidly damped law. The time constant was found to be 386 min and the total reduction of the parameter c was 0.04%. In the study of Kircher et al. [8], the 15 h-growth of T_c from 16 K (at $\tau = 1$ h) to 35 K for the $YBa_2Cu_3O_{6.35}$ sample and from 47 to 55 K for the $YBa_2Cu_3O_{6.45}$ was observed. The elevation of T_c was accompanied by increasing the Cu^+ concentration. The relaxation of the lattice parameter c occurring in the sample $YBa_2Cu_3O_{6.25}$ at RT was studied by Shaked et al. [5]. The resultant decrease in this parameter of ~0.0015 Å, reaching logarithmically with the relaxation time of ~760 min, was recorded. All these effects are often called *room-temperature aging effects*. The kinetics of the aging effect in $YBa_2Cu_3O_{6+\delta}$ with small deviations in the storage temperature from RT was studied by Veal et al. [7]. The strong dependence of the relaxation rate on temperature observed in this investigation indicated that processes underlying the aging effect are of thermally activated nature.

Typically, the changes in T_c and c observed after quenching $YBa_2Cu_3O_{6+\delta}$ are explained by the ordering processes proceeding in the incomplete oxygen sublattice of the CuO_δ plane at RT, Fig. 1(a). Herewith, it is generally accepted that T_c is greater, when the degree of oxygen ordering is higher [4–15]. In the general case, the oxygen ordering degree can be determined as the part of oxygen in the CuO_δ plane belonging to the chain fragments of type I, see Fig. 1(b), in which the copper ions are square-planar coordinated by oxygen and their formal valence state is Cu(III). Such fragments are considered [5,14–18] as a source of the hole formation unlike other types of fragments: II and III, see Fig. 1(b).

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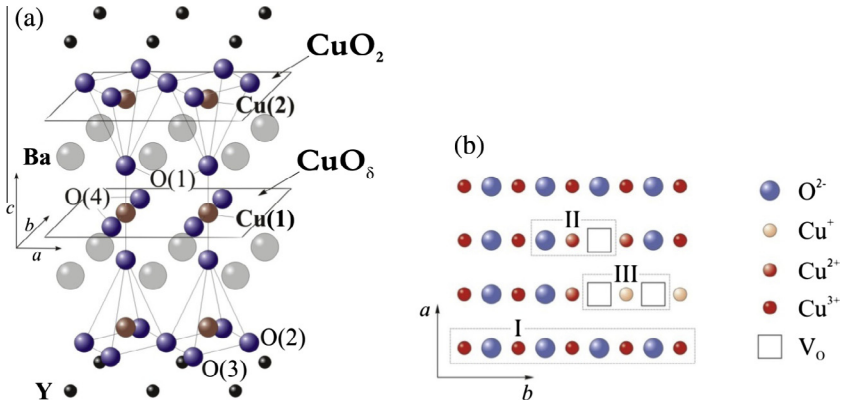

Fig. 1. (a) The crystal lattice of $YBa_2Cu_3O_{6+\delta}$; (b) schematic illustration of the CuO_δ plane in $YBa_2Cu_3O_{6+\delta}$ (*ab*0), within which ordering of oxygen ions occurs (Cu—O—Cu chains extended along the *b*-axis). Shown structure is named ortho-I phase. Highlighted fragments I, II and III correspond to different types of copper ion coordination. V_o denotes the oxygen vacancy.

Meanwhile, the hole concentration in CuO_2 planes [Fig. 1(a)], where superconductivity is realized, depends directly on the hole concentration in CuO_δ through the mechanism of charge transfer [14,17]. Using this model it is suggested that aging effects are controlled by the kinetics of an ortho-I → ortho-II transition occurring in $YBa_2Cu_3O_{6+\delta}$ at RT, where the ortho-I phase (see Fig. 1) likely to contain few copper ions in the chain fragments of type I is formed during high-temperature oxidation and the ortho-II phase (with alternating Cu—O—Cu and Cu—V_o—Cu chains along the *a*-direction of CuO_δ planes) arises at RT as thermodynamically stable superstructure and has a lot more Cu(III) ions. In turn, the mechanism of the time-dependent decrease in the parameter *c* is still under question. This problem was touched in [5] where the authors supposed the lattice parameters to be related to the charge transfer occurring between the CuO_δ and CuO_2 planes (as a consequence of oxygen ordering), like in the case of T_c.

To our knowledge, however, there are no direct evidences linking the aging effects with the realization of low-temperature superstructure orderings. Furthermore, more recent investigations provide convincing examples which are in poor agreement with this correlation. So, the kinetics of the ortho-I → ortho-II transition studied by X-ray diffraction [19,20] turned out to be characterized by the relaxation time (about 100 h at 70–75 °C) which is much longer than that typical for the kinetics of aging effects. Besides, in studies where comparative analysis of T_c was carried out on the ortho-II and ortho-I based samples with the same δ [13,21], a difference in T_c was found to be not more than 5 K for the entire range of compositions examined. By annealing samples in the range 25–120 °C (in order to vary their ortho-II ordering degree), a maximum difference in T_c amounted to only 2 K ($51 \leqslant T_c \leqslant 53$ K) [22]. Finally, the enthalpy of the disproportionation reaction.

$$Cu^{2+} \rightarrow Cu^{+} + Cu^{3+}, \tag{1}$$

which controls the aging effects [according to Knizhnik et al. [3], this enthalpy is about 10 kJ/(mol $YBa_2Cu_3O_{6+\delta}$)] is too large to pertain to the "driving force" of the ortho-I → ortho-II transition (interactions playing a leading role in this transition are of order 1 kJ/(mol $YBa_2Cu_3O_{6+\delta}$) [23]). This is the thermodynamic support for the findings [13,21] that proper values of T_c can be achieved without necessity for the ortho-II structure to be formed.

Thus, the nature of the aging effects cannot be considered as fully clarified. The problem is complicated by deficiency of the information on changing concentration of holes with time at RT. Currently, available estimates are not numerous and do not agree well with each other.

In order to suggest a new explanation for the room-temperature aging effects, XPS data about the chemical state of oxygen in $YBa_2Cu_3O_{6+\delta}$ and the lattice parameters vs δ detailed experimental dependences have been obtained for different values of post-quench time τ. We based on a reasonable assumption that the change of the lattice parameter *c* occurring over time must directly reflect the process of the charge transfer between the planes CuO_δ and CuO_2. This assumption allows analyzing the δ- and τ-dependent hole concentration in the CuO_2 plane and juxtaposing it with the chemical state of oxygen in $YBa_2Cu_3O_{6+\delta}$ showing clearly the presence of holes on a part of oxygen at $\tau \rightarrow 0$ and their disappearance later on. As a result, we have suggested a new mechanism for changing the hole concentration in the CuO_2 plane independent from oxygen ordering in $YBa_2Cu_3O_{6+\delta}$.

2. Experiment details

$YBa_2Cu_3O_{6+\delta}$ was synthesized from the oxides Y_2O_3, CuO and barium carbonate $BaCO_3$, which were mechanically mixed and annealed at 950 °C for 100 h. As a result, single phase product of the tetragonal structural modification was formed. To obtain samples with different oxygen content, portions of the synthesized material (by ~5–6 g) were oxidized at different temperatures from the interval 470 to 950 °C in air atmosphere and then quenched. The duration of oxidative annealing ranged from 1.5 to 2.5 h depending on the temperature of the process. The uniform distribution of oxygen throughout the material volume was achieved by repeated oxidation of the samples at the same thermodynamic parameters (*t*, p_{O2}). However, the heat treatment was conducted now in crucibles partially covered with lids. To avoid additional oxidation of the samples during their cooling, crucibles with samples were fully closed before the quenching procedure. Material for research was taken from the central part of the sintered sample.

The oxygen content was monitored by the change in mass of a small portion of the sample during additional 1 h oxidation at 470 °C in air. Using the values of Δm, the initial composition of a sample was determined by the formula:

$$6 + \delta = 6.9 - \left[\frac{2.43 \cdot m}{\Delta m}\right], \tag{2}$$

where 6.9 is the oxygen content in $YBa_2Cu_3O_{6+\delta}$ corresponding to the conditions of its additional oxidative annealing (t = 470 °C, p_{O2} = 21 kPa, τ = 1 h); *m* – mass of the sample. There was a good correlation between δ values calculated by Eq. (2) and conditions of oxidative annealing (at least for samples with orthorhombic structure), the relationship between which was established in the study