Oxygen inhomogeneities in $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ single crystals with $x > 0.5$ (oxygen inhomogeneities in $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}\dots$)

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Abstract. The microstructure of HTS $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ single crystals with $x \geq 0.5$ has been investigated by TEM and selected area diffraction. An inhomogeneous oxygen distribution over the crystal was observed. Large differences between the bulk crystal structure and the surface have been established. The bulk structure was presented by orthorhombic blocks ($\approx 100 \times 10 \times 20$ nm in size) embedded in tetragonal matrix with $x \approx 1$. The bulk structure was not of a superconductive type. The crystal surface was enriched by oxygen and had the usual orthorhombic twinned structure. The superconductive properties of the whole specimen were determined by surface layer about $5 \mu\text{m}$ thick.

Keywords. Superconductivity; single crystal; $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$; transmission electron microscopy.

1. Introduction

It is now well established that the superconductive properties and crystal structure of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ are strongly dependent on the oxygen content x (see, e.g. Cava *et al* 1987; Jorgensen *et al* 1987; Freitas and Plaskett 1987; Kishio *et al* 1987; Kubo *et al* 1987; Takayama-Muromachi *et al* 1987; Tokumoto *et al* 1987; Stoffel *et al* 1987). To resolve this problem experimental methods for obtaining crystalline samples with different x were developed (see, e.g. Verweij *et al* 1989; Yguchi *et al* 1988) and the distribution of oxygen ions in crystal lattice was investigated (see, e.g. Aligia *et al* 1988; Cava *et al* 1987; Couach *et al* 1988; Hiraga *et al* 1987; Hodeau *et al* 1988; Kotyuzhanskii and Svistov 1988; Matsui 1987; Matsui *et al* 1987; Molchanov *et al* 1989; Nakamura and Ogawa 1988; Verweij 1988; Welch *et al* 1987; Zandbergen and Thomas 1988). But some questions are not completely clarified up to now. For example a series of contradictory results concerning electrical and other properties were reported for crystals with low oxygen content (see, e.g. Cava *et al* 1987; Monod *et al* 1987; Mydosh 1987; Sawada *et al* 1987; Wang *et al* 1987). It is also unclear up to now whether oxygen is distributed homogeneously in crystals with $0.5 \leq x \leq 1$, or whether it forms orthorhombic (with $x = 0.5$) and tetragonal (with $x = 1$) regions (see, e.g. Molchanov *et al* 1989). The main object of this paper is to investigate the electrical properties and the real crystal structure of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ single crystals with low oxygen content.

2. Experiment and specimens

Single crystals of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ with $x = 0.7$ and dimensions $1 \times 1 \times 0.03 \text{ mm}^3$ were grown by the method described in Bykov *et al* (1988). After the crystals were grown they were very quickly cooled in air. The average oxygen content was determined with accuracy $\Delta x = \pm 0.05$ by X-ray measurement of unit cell parameter c (see, e.g. Cava *et al* 1987). These measurements were carried out on a X-ray single crystal diffractometer

using (006) Bragg reflection. The crystals characterized by Bragg peak width less than $6'$ were selected for further investigation. To analyse the oxygen distribution in superconductive crystals, transmission electron microscopy (TEM) and electron selected area diffraction (SAD) have been used. The specimens for TEM were thinned by ion milling. Final thinning employed was 4 kV, ≈ 15 mA Ar^+ ion beams incident at a shallow angle ($\approx 15^\circ$) to prevent oxygen loss due to specimen heating. At the beginning a single crystal was thinned on one side only to study the surface structure. Later this crystal was thinned on the other side to investigate the bulk structure. The surface structure of the specimens was also investigated by optical microscopy in reflection polarized mode.

Superconducting properties of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ crystals were measured using LC-generator at frequency $f_0 \approx 10$ MHz. The investigated specimens were attached to the glass rod which could be moved relatively to the induction coil. The sample was oriented relatively to the magnetic field to induce electrical current in the (001) plane. The frequency shift of the LC-generator followed the specimen transition to the superconductive state. The specimen and induction coil were placed in a copper capsule which could be moved up and down above the liquid He surface. By doing this we could vary the temperature of the sample within a wide region 4.2–300 K. The temperature was measured by a thermocouple. To prevent heating of the specimen by the induced current the LC-generator operated in a pulse mode. The pulse duration was about 1 ms and the time interval between two successive pulses was about 1 s.

Figure 1. [001] TEM image of the bulk crystal structure; SAD pattern is inserted.

3. Results and discussion

The TEM study revealed that real crystal structures of the bulk material and surface crystalline layers (about several microns thick) are completely different. A typical image of the bulk structure is shown in figure 1. One can see the network of blocks elongated in two orthogonal directions $[110]$ and $[\bar{1}10]$. In (001) SAD patterns one could clearly observe streaks in $[110]$ and $[\bar{1}10]$. The length of these streaks corresponds to block width of about 8–10 nm. The diffraction contrast observed is connected with elastic strain field created by the blocks. In the $[001]$ direction the crystal is divided into thin layers of about 20 nm thick characterized by different values of the c -parameter measured in HRTEM images (figure 2). Moreover, as revealed by HRTEM, the cation sublattice is not distorted in these layers. So, one can conclude that the bulk crystal structure consists of $100 \times 10 \times 20 \text{ nm}^3$ blocks embedded in a matrix. As these parallelepipeds are arranged in two orthogonal directions $[110]$ and $[\bar{1}10]$, one can conclude that these directions are equivalent to each other and the matrix is tetragonal. In HRTEM images taken in $[001]$ one can observe mainly two types of regions. One is characterized by ordered chains of O-vacancies giving rise to the doubling of the unit cell parameter a (figure 3), while the other has no such ordering. The average oxygen content is $x \approx 0.7$ and in the ordered regions $x \approx 0.5$ (see, e.g. Zandbergen and Thomas

Figure 2. $[100]$ HRTEM image of the bulk crystal structure. The blocks with different c unit cell parameters are clearly seen.

Figure 3. [001] HRTEM image of the bulk crystal structure. The doubling of the unit cell parameter a is marked.

1988) and therefore one can conclude that in the rest matrix $x \approx 1$. Thus the bulk crystal structure is not homogeneous but consists of regions with tetragonal ($x \approx 1$) and orthorhombic ($x \approx 0.5$) structures. This type of structure was observed at any distance from the crystal surface except a very thin ($< 5 \mu\text{m}$) surface layer. It is quite natural that the thin surface crystal layer is saturated by oxygen during quenching from $\approx 1200 \text{ K}$ in air. The thickness of this layer is determined by the cooling rate.

In the surface layer two types of interchangeable lamella (18–20 nm and 40–48 nm width correspondingly) running in $[110]$ were observed (figure 4). The interlamella boundary width measured in HRTEM images and SAD patterns is approximately 7–9 nm. In SAD patterns one could clearly observe the splitting of reflections due to the orthorhombic twinning (figure 4). The local oxygen content $x \approx 0.35$ was determined from SAD orthorhombic distortion parameter measurements (see e.g. Cava *et al* 1987). The HRTEM images of crystal structures in A and B regions are shown in figure 5. In B lamella one can observe the contrast from ordered O-vacancies giving rise to the doubling of the unit cell parameter a . As a result of this ordering in SAD there appear the diffuse maxima. As mentioned earlier it means $x \approx 0.5$. In the A region such a contrast is missing, so one can suppose that $x \approx 0$. This local oxygen distribution is in good agreement with the average x value determined earlier ($\bar{x} \approx 0.35$).

The results of surface structure investigations in reflected polarized light are in good agreement with HRTEM data. The specimen surface looks like optically isotropic after ion milling (bulk structure). This can be explained by the poor optical microscope

Figure 4. [001] TEM image of surface crystal structure; SAD pattern is inserted; Two types of lamellae are arrowed by A and B.

resolution to observe the orthorhombic blocks of about 10 nm in size (figure 1). Thus the “average” bulk structure is tetragonal. As-grown crystal surface consists of orthorhombic regions (see, e.g. Schmid *et al* 1988) orthogonal to one another and according to HRTEM formed by $[110]$ and $[\bar{1}10]$ lamellar structure correspondingly.

It is well known that quite a long annealing of a crystal in He atmosphere at $T \leq 670$ K (see, e.g. Aleksandrov *et al* 1988) gives rise to the disappearance of superconductivity in quenched $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ crystals at $x \geq 0.5$, while lowering of average $\bar{x}$ determined by X-ray measurements is less than 0.01. To understand this result some crystals were annealed for 64 h at $T = 640$ K in air. HRTEM revealed that the bulk crystal structure was not significantly changed after this procedure. The frequency shifts of LC-generator are shown in figure 6 as a function of temperature for different specimen treatments (initial, annealed, initial ion milled from both surfaces). These results can be explained assuming that superconductivity of the initial crystal is controlled by oxygen-saturated surface layer. This explanation is in good agreement with the TEM observations.

The observed oxygen inhomogeneities are apparently determined by some effective interaction between oxygen vacancies giving rise to cluster formation (see, e.g. Aligia *et al* 1988; Hodeau *et al* 1988; McKinnon *et al* 1988). This interaction can be explained by the tendency of the crystal to minimize the number of three oxygen-coordinated Cu^+ cations.

Figure 5. [001] HRTEM images of crystal structure in A and B regions.

Figure 6. Temperature dependences of LC-generator frequency shifts for different specimen treatments: ○-initial sample, △-initial sample milled from both surfaces by ion beam, ◇-initial sample milled from both surfaces by ion beam and then annealed in oxygen, □-initial sample annealed in air.

Our results are in good agreement with X-ray structure analysis data reported for quenched crystals (see, e.g. Molchanov *et al* 1989). But this contradicts with the results of Molchanov *et al* (1989), where a conclusion about the existence of only two types of blocks with $x = 1$ and $x = 0.5$ were made, x value varying continuously in the interval $0.5 \leq x \leq 1$.

Taking into account the oxygen distribution inhomogeneities one can easily explain the rather high dispersion of electrical properties observed by a number of authors (see e.g. Cava *et al* 1987; Monod *et al* 1987; Mydosh 1987; Sawada *et al* 1987; Wang *et al* 1987). Some properties of HTS at $x \geq 0.5$ can be explained by oxygen inhomogeneities. For example, the singularity in $T_c(x)$ at $x \approx 0.5$ can be brought about not only by electron subsystem, but also by percolation effects.

To interpret the electrical properties it is necessary to consider the enrichment of the surface crystal layer by oxygen. This effect gives rise to the formation of a very thin superconductive layer on the nonsuperconductive crystalline matrix and can be used in practice for the creation of quasi-two-dimensional electronic superconductive devices.

References

- Aleksandrov I V, Bykov A B, Zibrov I P, Makarenko I N, Mel'nikov O K, Molchanov V N, Muradyan L A and Nikiforov D V 1988 *Pis'ma Zh. Eksp. Teor. Fiz.* **48** 449; *JETP Lett.* **48** 493
- Aleksandrov I V, Volodin A P, Makarenko I N, Svistov L E and Stishov S M 1988 *Pis'ma Zh. Eksp. Teor. Fiz.* **49** 287; *JETP Lett.* **49** 327
- Aligia A A, Rojo A G and Alascio B R 1988 *Phys. Rev.* **B38** 6604
- Bykov A B *et al* 1988 *J. Cryst. Growth* **91** 302
- Cava R J, Ballogg B, Chen C H, Rietman E A, Zahurak S M and Werder D 1987 *Phys. Rev.* **B36** 5719
- Couach M *et al* 1988 *Physica* **C153–155** 844
- Freitas P P and Plaskett T S 1987 *Phys. Rev.* **B36** 5723
- Hiraga K *et al* 1987 *J. Electron. Microsc.* **30** 261
- Hodeau J-L *et al* 1988 *Physica* **C153–155** 582
- Iguchi I, Sugushita A, Yanagisawa M, Iguchi I, Hosaka S, Yokoyama Y and Asano H 1988 *Jap. J. Appl. Phys.* **27** 992
- Jorgensen J D, Veal B W, Kwok W K, Crabtree G W, Umezawa A, Nowicki L J and Paulikas A P 1987 *Phys. Rev.* **B36** 5731
- Kishio K, Shimoyama J, Hasegawa T, Koichi K and Kazuo F 1987 *Jap. J. Appl. Phys.* **26** L1228
- Kotyuzhanskii B Ya and Svistov L E 1988 *Pis'ma Zh. Eksp. Teor. Fiz.* **47** 317; *JETP Lett.* **47** 381
- Kubo Y, Nakabayashi Y, Tabuchi J, Yoshitake T, Ochi A, Utsumi K, Igarashi H and Yonezawa M 1987 *Jap. J. Appl. Phys.* **26** L1888
- Matsui Y 1987 *Jap. J. Appl. Phys.* **26** 2021
- Matsui Y, Takayama-Muromachi E, Ono A, Horiuchi S and Kato K 1987 *Jap. J. Appl. Phys.* **26** L777
- McKinnon W R, Post M L, Selwyn L S, Pleizier G, Tarascon J M, Barbour P, Greene L H and Hull G W 1988 *Phys. Rev.* **38** 6543
- Molchanov V N, Muradyan L A and Simonov V I 1989 *Pis'ma Zh. Eksp. Teor. Fiz.* **49** 222; *JETP Lett.* **49** 257
- Monod P, Ribault M, D'yvoire F, Jegourdez J, Collin G and Revcolevschi A 1987 *J. Phys. (France)* **48** 1369
- Mydosh J A 1987 *J. Phys. B. Cond. Matter* **68** 1
- Nakamura K and Ogawa K 1988 *Jap. J. Appl. Phys.* **27** 577
- O'Sullivan J M and Chang B P 1988 *Appl. Phys. Lett.* **52** 1441
- Sawada H, Iwazumi T, Saito Y, Abe Y, Ikeda H and Yoshizaki R 1987 *Jap. J. Appl. Phys.* **26** L1054
- Schmid H *et al* 1988 *Physica* **C153–155** 1748
- Stoffel N G, Tarascon J M, Chang Y, Onellion M, Niles D W and Margaritondo G 1987 *Phys. Rev.* **B36** 3986
- Takayama-Muromachi E, Uchida Y, Ishii M, Tanaka T and Kato K 1987 *Jap. J. Appl. Phys.* **26** L1156
- Tokumoto M, Ihara H, Matsubara T, Hirabayashi M, Terada N, Oyanagi H, Murata K and Kimura Y 1987 *Jap. J. Appl. Phys.* **26** 1565

Verweij H 1988 *Solid State Commun.* **67** 109

Verweij H et al 1989 *J. Phys. Chem. Solids* **50** 75

Wang Z Z, Clayhold J, Ong N P, Tarascon J M, Greene L H, McKinnon W R and Hull G W 1987 *Phys. Rev.* **B36** 7222

Welch D O, Emery V J and Cos D E 1987 *Nature (London)* **327** 278

Zandbergen H W and Thomas G 1988 *Phys. Status Solidi* **107** 825