Electric-current-stimulated diffusion of heavy ions and oxygen in YBCO (123) and Bi (2223) HTCS films at 4.2 - 300 K

E.N. Lubnin, G.N. Mikhailova, A.M. Prokhorov, A.S. Seferov, A.V. Troitskii, D.G.Andrianov*, S.O.Klimonskii*

General Physics Institute RAS, Vavilov str. 38, Moscow 117942, Russia

* State Institute of Rare Metals, Moscow, Russia

ABSTRACT

The results of the study of electrostimulated diffusion in polycrystalline and epitaxial YBCO (123) and ceramic Bi (2223) HTCS films give evidence of the motion of heavy ions and oxygen under the transport superconducting current flow.

Long-duration d.c. flowing in films in the superconducting state at 4.2 and 77 K leads to new morphological forms with modified chemical composition, formation of nonsuperconducting phases. The effect in the high-quality epitaxial films exists, but it is weaker.

Long-duration flowing of high-power 36 GHz current leads to formation of periodic strip structures enriched with copper and oxygen. The experiments with thick (25 μm) Bi (2223) films reveal modified stoichiometry practically over the entire film. At 300 K the YBCO (123) system is shown to have the ionic conduction component. Possible mechanisms of the observed experimental effects are discussed.

1. INTRODUCTION

Experimental study of the samples of oxide HTCS showed that their initial characteristics are unstable and modified under the action of different chemical and thermal factors[1-3], deformations[4], long-duration current flowing at high temperatures[5]. The causes of these phenomena are different, but they seem to be connected not only with imperfect technologies of manufacturing the samples, but also with specific features of crystallochemical structure of these substances[6,7].

We payed attention that owing to its crystallochemical properties, the YBaCuO system reminds superionic conductors much more than stable stoichiometric oxides. The transport of ions caused by the current flow in such a structure may lead to the formation of crystallochemically stable compounds. We presumed that these properties may hold also in the superconducting state. Experiments confirmed this supposition and for the first time the electrochemical reaction in the superconducting film was observed at 4.2 K[8,9].

In there experiments[8,9] we used polycrystalline films (with weak links between superconducting granules) and the effects were easily observed, but later the same effects were discovered at higher-quality samples of Y[10]-, Bi[11]- and Tl-based systems[12], Y-ceramics[13] with specific features dependent on temperature (at lower temperatures the effect is smaller), structural perfection (the strongest modification occurs in granular ceramic samples and polycrystalline nonoriented films), current frequency.

The phenomenon of electrostimulated diffusion seems to be inherent in HTCS systems and its study is important from the fundamental and practical point of view.

2. SAMPLES AND METHODS OF INVESTIGATION

We studied polycrystalline YBCO (123) films 2 – 3 μm thick on (YSZ) substrates obtained by the condensate – diffusion method, textured epitaxial films on MgO and $LaAlO_3$ substrates obtained by magnetron sputtering and laser deposition, and Bi (2223) ceramic films on Ag substrates.

The samples had 4 indium contacts. The inner ones were used for potential measurements, and through the outer contacts the transport superconducting current was passing for many hours (days). The samples were placed in an ampule filled with gaseous helium at the atmospheric pressure plunged into liquid helium or nitrogen.

Scanning electron microscopy, energy – dispersive X – ray microanalysis (Camscan – 4, EDX Link), diffractometry, Auger – spectrometry, statistical analysis were applied to the film characterization and comparison with the reference samples. Dependences $R(T)$ were measured by the 4-probe resistive method.

3. FIRST RESULTS ON THE ELECTROSTIMULATED MODIFICATION OF SUPERCONDUCTING FILMS AT 4.2 K

Here we briefly describe the experimental results[8,9], where for the first time the modified chemical composition and film morphology were observed under the influence of long – duration superconducting transport current flowing.

The experiments were carried out at polycrystalline $Y_1Ba_2Cu_3O_{7-x}$ films about 3 μm thick. The analysis showed them to be homogeneous and single – phased, with the grain structure (3 – 5 μm in size) and nonoriented c – axis.

The superconducting current lower than the critical one ($I = 0.3I_c$) was passing through the sample with the 2 dimensions of 12 x 5 mm^2 for 166 hours, and the charge transferred through the film was 2.7×10^4 C. After that the parameters of the superconducting transition remained practically unchanged.

To characterize the film morphology and composition before and after the experiment, SEM Camscan – 4 with the energy dispersive X – ray analysis (EDX Link) was used.

The phase contrast in the reference sample is uniform, the surface is smooth. After the current flowing a "road" with an irregular surface was formed between the electrodes. The phase contrast of the experimental sample is nonuniform, scaled formations with sizes of 1 – 20 μm are observed mainly near electrodes.

The total composition was determined on the areas of 300 $\times$ 300 μm near the electrodes and in the center. The content of Cu was higher by 4 – 6 wt.% in the initial film than after

Fig. 1. Microphotograph (BEI) of the initial YBaCuO (123) film. The mean grain size is 3–5 μm.
Fig. 2. Microphotograph (BEI) of the modified area of (123) at 77 K.

the experiment (the relative error was 2%) and by 2–3 wt.% for Ba. The local composition was studied with the a spatial resolution of 1 μm. In the initial sample a high homogeneity was found, and after the current flowing point formations with $CuBaO_2$ composition were revealed. In addition, statistical processing of the results showed that the region near the negative electrode is enriched with Cu by 4 wt.% in comparison with the positive one. In some areas the Cu concentration was up to 38 wt.%. That was the first evidence of the mass transfer accompanying the superconducting current.

4. ELECTRODIFFUSION OF HEAVY IONS IN YBaCuO AT 77 K COMPARISON OF POLYCRYSTALLINE AND EPITAXIAL FILMS[10]

It was important to investigate the stability of HTCS films at 77 K, because this is the working temperature for the HTCS devices. From the technological point of view the stability of HTCS is the key problem. The experiment was carried out in the same scheme. The samples similar to those studied at 4.2 K were studied at 77 K (see Fig. 1). The studied and reference polycrystalline samples were mounted at $T = 77$ K at helium atmosphere close to each other. The d.c. of 1 mA (0.3 j_c) was passing during 575 hours. Before and after the experiment the characteristic of the superconducting transition $R(T)$ was measured, and the composition and morphology studies were performed. The effect at 77 K for polycrystalline films is shown in Fig. 2. The formation of needle–like crystals is rather homogeneous over the whole sample. The superconducting transition curve remained practically unchanged indicating that nonsuperconducting phases do not entirely block the film cross section.

Similar experiment was carried out for epitaxial textured films 0.5 μm thick on MgO substrates obtained by magnetron sputtering in oxygen. The disorientation in c–plane was within 1° , in ab–plane — 2.5°, j_c (77 K) = 10^6 A / cm^2. The resistance of aluminum electrodes with vanadium sublayer was $\sim 10^{-2}$ Ohm. The current density $j < j_c$ was passing for 70 hours through the film, which was controlled to stay in the superconducting state. The charge of 10^5 C was transferred. As a result, the migration of Cu and O ions to opposite electrodes was found (see Fig. 3).

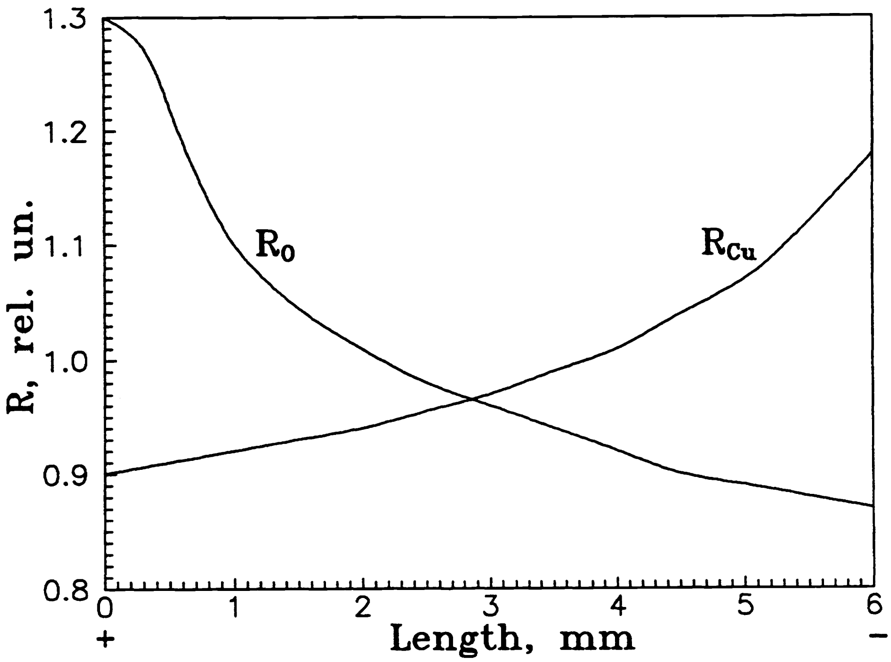

Fig. 3. Spatial distribution of Cu and O in the epitaxial (123) film after d.c. flowing. $R = 1$ corresponds to the stoichiometric concentration.

In contrast to the case of polycrystalline films, the surface modification of epitaxial ones are not so dramatic. The migration process leads to the change of specific volume of grains. Their boundaries become deeper, and the film – more porous (from 100 nm to 150 nm) (see Fig. 4 and 5).

The study of high-quality thin and narrow (bridge-type) epitaxial films (laser deposition, $100\,\mu\text{m}\times 0.24\,\mu\text{m}$ $j_c = 3 \times 10^6\,\text{A}/\text{cm}^2$) revealed a modification of the superconducting transition curve. After the charge $Q \approx 10^5$ C passed through the film, a step appeared in the transition curve (Fig. 6).

Thus the diffusion and decomposition effects exist also in quasi-monocrystalline films, but they have specific features. This study shows that the problem under consideration is complex, and we must distinguish the fundamental crystallochemical factors and the causes connected with the structural perfection, intergrain boundaries and other mechanisms.

5. DECOMPOSITION PROCESSES IN A HIGH-POWER MICROWAVE FIELD

Analyzing the probable causes of ion the diffusion in the superconducting state, we may suspect the electrodes to be sources of heating and gradual destruction of superconductivity of separate grains and development of superionic processes. Therefore, it was important to study these effects by contactless methods at the microwave frequencies. In addition, the application of HTCS elements as microwave devices demands detailed investigation of electrostimulasted diffusion of ions in this field.

Fig. 4. Surface microphotographs of the epitaxial film before current flowing at 77 K. The area is $8 \times 11\ \mu m^2$.

In the microwave field the absorption always exists even in usual superconductors (LTCS), because the alternative motion of carriers is always connected with the internal electric field. For instance, estimates show that at $f = 50$ Hz and $I = 1$ A the internal electric field is $E_i = 10^{-12}$ V / cm. With the diminishing T the microwave absorption decreases, because the number of absorbing normal carriers reduces.

The film (123) YBCO under study on a single-crystal $LaAlO_3$ substrate was $0.3\ \mu m$ thick with the size of $8 \times 10\ mm^2$, $T_c = 84$ K, $j_c = 10^4$ A / cm^2 (this film was obtain by method of magnetron deposition). It replaced a part of the wide wall of the microwave resonator, and the microwave current much lower than the I_c was flowing through the film for 30 hours at $T = 77$ K. The generated microwave power was 5 W at the frequiency of 36 GHz.

As a result, convex formations $\sim 2\ \mu m$ sized with prevailing light elements (Cu, O) and new strip periodical structures (Fig. 7) with a period of $\sim 10\ \mu m$ were formed[14]. Superconducting properties were not lost, although j_c became lower — 10^3 A / cm^2. These results can be treated within the framework of a new spatial-time model of a dissipationless current flow[15] that leads to an anomalous ion diffusion from the current-carrying regions, formation of Cu- and O-enriched phases and their "freezing", which are experimentally observed. The spatial parameter deduced from this theory is close to the period of the experimentally observed structures.

6. RECRYSTALLIZATION AND IN-SITU EXPERIMENTS IN YBaCuO FILMS AT 300 K UNDER D.C. FLOWING

In order to study the current-carrying properties of the YBCO (123) system in nonsuper-

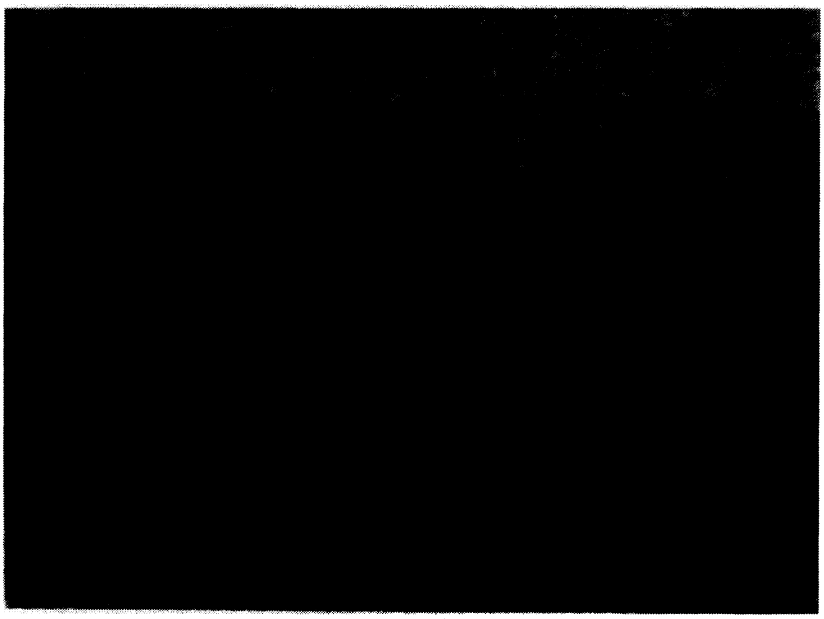

Fig. 5. Surface microphotographs of the epitaxial film after current flowing at 77 K. The area is $8 \times 11\ \mu m^2$.

conducting state we performed the experiments at 300 K. As was already mentioned, chrystallochemical properties of new oxide superconductors are close to solid electrolites, and this determines a mixed character of their conductivity and its ion component. It was expected that during the superionic current flow the forming crystallochemically stable compounds may block the current channels, and this should result in an inhomogeneous distribution of new phases between the electrodes. In addition it was necessary to measure the diffusion characteristics of this material.

The samples of YBaCuO similar to those studied at 4.2 K were studied at 300 K (see Fig. 1). The resistance of the film and the summary resistance of two contacts were 43 and 3 Ohm, respectively. The direct current of 28 mA ($j = 600\ A/cm^2$) was passing through the film during 336 hours.

In contrast to the reference sample that remained unchanged, in the experimental one a boundary dividing the regions of the positive and negative electrodes appeared approximately in the center. Near the positive electrode there appeared needle-like, prismatic and triangular crystals resembling those at 77 K (see Fig. 2). New phases – Y_2BaCuO_x, $YBa_2Cu_3O_y$, $BaCuO_z$, CuO_5 – were revealed by X-ray spectral measurements in the modified film areas. Near the negative electrode the film morphology and chemical composition remained unchanged.

In the second experiment with the similar sample (transport current density was 3×10^3 A/cm^2) the total charge transfer was 2.9×10^3 C. Periodically the current was switched off and the sample was measured by the four-probe method. It was found that the film resistance was

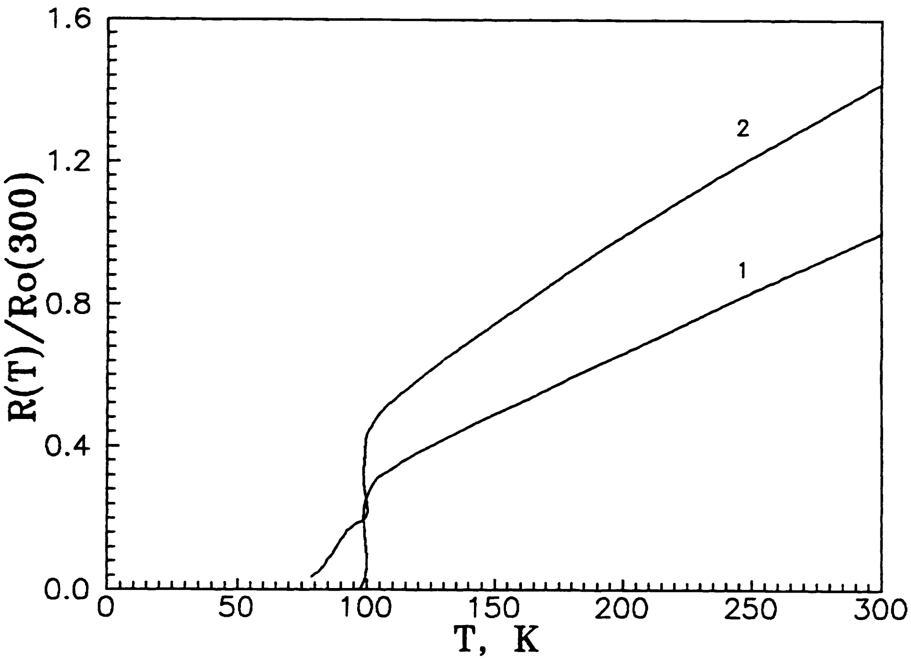

Fig. 6. Temperature dependences $R(T)$ for a high-quality epitaxial film 0.3 μm thick before (*1*) and after (*2*) current passing at 77 K.

growing as a function of the transferred charge from 24 up to 35 Ω

In-situ SEM experiments showed that at a short-duration current flowing (0.5 s, 300 mA) through two needle electrodes applied to the film with the distance of 0.5 mm between them the region of the positive electrode is enriched with Cu.

Using local heating of various parts of the film up to 600 K with the help of electron beam we estimated the thermodiffusion coefficient D for Cu ions, which varied within a large range from 10^{-3} to 10^{-8} $cm^2 \cdot s^{-1}$ in different probed areas. Such a spread of D, in our opinion, is due to the film inhomogeneity and presence of carbon impurities on its surface.

The obtained results show a high ion mobility in (123) film at room temperature. Essential morphological modifications of the film surface and large distance of the ion transfer may indicate that this process in YBaCuO film is realized not by the usual thermodiffusion mechanism. The results of this study confirmed a mixed character of the conductivity and an essential contribution of the ionic component.

7. ELECTROSTIMULATED DIFFUSION IN $(Bi,Pb)_2Sr_2Ca_2Cu_3O_8$ HTCS FILMS AT 4.2 K[17]

Bi-based HTCS are of special interest being chemically more stable than YBCO material. They have high critical parameters and are promising for high-power current application, such as creation of superconducting cables and wires. The films under study were prepared by depositing the superconducting powder on silver substrates with subsequent cyclic pressing, rolling

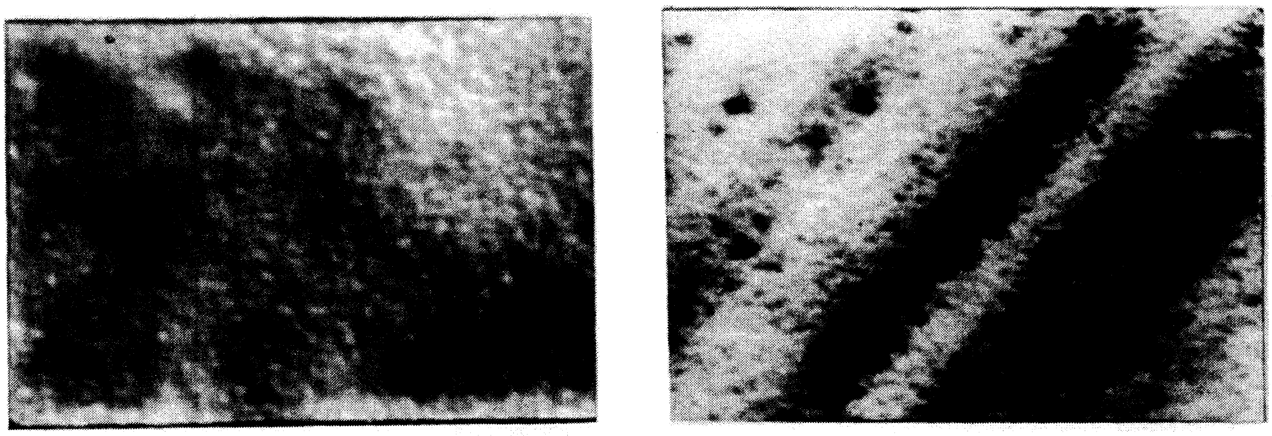

Fig. 7. SEM microphotographs of HTCS (123) film before (*a*) and after (*b*) the microwave current flowing at 77 K. The area is 30 × 40 μm^2.

and annealing[16]. Their characteristics and size are: $T_c = 105\,K$, $j_c \sim 900\,A/cm^2$ (77 K, 20 Oe) and 3300 A/cm^2 (12 K, 20 Oe), $10 \times 5\ mm^2$, $\sim 25\mu m$ thick. The ampule containing two similar samples was filled with heat-exchange helium and plunged into liquid helium. After the d.c. flowing in the superconducting state for 400 hours at 4.2 K remarkable changes in the initial film composition and surface morphology were found. X-ray spectral microanalysis reveals small areas of chemical inhomogeneities including Ca_2CuO_3 . Quantitative statistical characteristics of inhomogeneities accumulated on the film surface in the course of current flowing are obtained.

Fig. 8 shows the resultant morphology of Bi (2223) film[17] (SEM, secondary electrons, charge transferred $Q = 31500\,C$). Needle-like particles present a new phase Ca_2CuO_3. Dark regions are depleted of heavy elements.

The phase composition before and after current flowing was determined by diffractometry with the subsequent identification of phases with standard diffractograms for HTCS phases.

Chemical inhomogeneities, volume fractions of phases were determined using the statistical method of X-ray microanalysis (Camebax-Micro).

The initial films are smooth. The prevailing phase is the tetragonal modification of (2223) phase. The identified phases are: CuO, SrO, Bi_2O_3 and (2223) — 85%. As a result, a more precise composition of the initial film is determined: $Bi_{1.7}Pb_{0.2}Sr_{1.7}Ca_{1.8}Cu_{2.5}O_{8.5}$. To obtain more detailed data on chemical inhomogeneities that appeared after the superconducting current flowing we used statistical processing of the results of X-ray spectral microanalysis and showed that the modifications of the initial chemical composition are accumulated over the entire film. To construct the correlation matrix, we calculated the coefficients of linear correlation for pairs

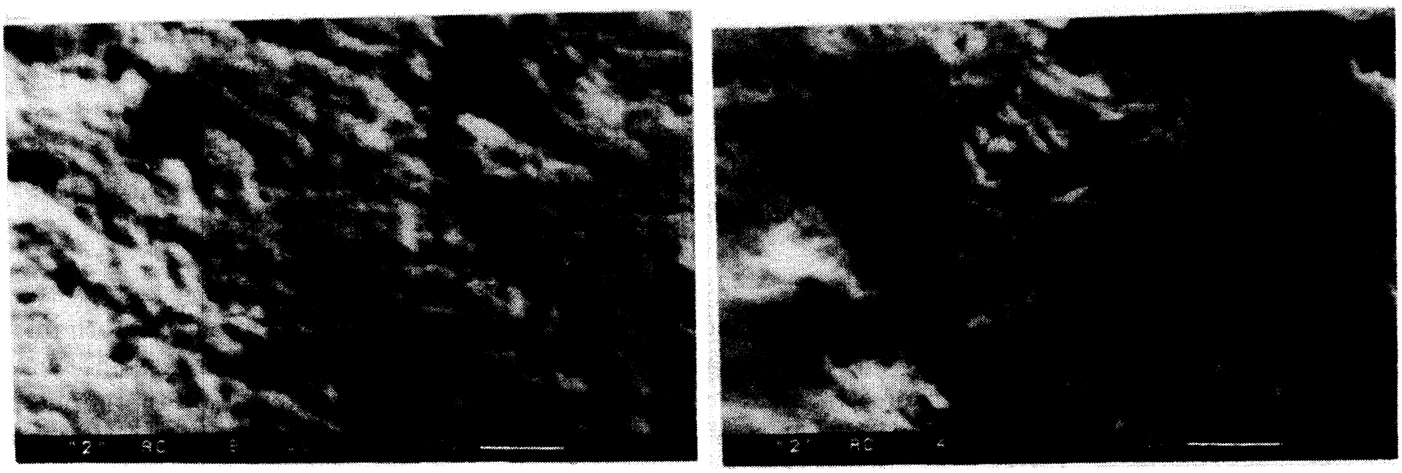

Fig. 8. SEM microphotograph (secondary electrons) of a section of Bi (2223) ceramic film surface before (*a*) and after (*b*) 440 hours of transport superconducting current flowing at 4.2 K. Needle–like particles belong to a new Ca_2CuO_3 phase. Dark regions are depleted of heavy elements.

of elements:

$$r_{i=1}^{N}(A,B) = \sum (I_i^A - I_m^A)\cdot(I_i^B - I_m^B)/(N-1)\cdot S^A \cdot S^B$$

where I_i^A , and I_m^A are the intensity at i–th point and the mean intensity, S^A is the r.m.s. deviation for the element A, $N = 400$.

Correlation matrix for Bi (2223) film after current flowing at 4.2 K

	Bi*	Sr	Ca	Cu
Bi	-	-0.428	0.631	0.528
Sr	-0.428	-	-0.419	-0.714
Ca	0.631	-0.419	-	0.374
Cu	0.528	-0.714	0.374	-

$N = 400$; Significance level 0.1 %

The negative signs of the correlation coefficients indicate mutually inverse variations of concentrations for pairs of elements with respect to the initial film, for which $0 < r < 1$. This means that the initial film is homogeneous in most of its microvolumes in contrast to the structure modified during the experiment, when the film stoichiometry becomes strongly violated.

The obtained results show that the electrostimulated diffusion of heavy ions discovered in YBCO (123) films exists also in Bi (2223) films.

8. THEORETICAL ASPECTS OF THE PROBLEM

For the present there is no consistent theories explaining the observed effects of the electrostimulated ion motion in HTCS at superconductive state. Additional difficulties are connected with the fact that as a rule theories developed for ideal models are compared with the experiment performed at quasi- single- crystals or polycrystalline samples with weak links between granules. Theoretical studies[6,7] of crystallochemical stability of oxide HTCS predicted the possibility of the displacement of oxygen and heavy ions during the current flowing at low temperatures. The structure of YBaCuO (123) has a sublattice of Cu^{2+} ions with a low energy barrier for the ion motion between partially occupied positions. Crystallochemical calculations show that such a system is unstable relative to the displacements of Cu^{2+} and O^{2-} ions to the distances comparable with the elementary cell, and the problem of motive forces is important for understanding the nature of the phenomena under consideration.

The problem of motive forces is not yet clear, especially at 4.2 K when the film is not overheatied and remains superconducting. It is almost obvious that the forces have electric origin, because the experimental pictures near positive and negative electrodes are different, and we come to a hypothesis that an electric field exists in the bulk of oxide material in the superconducting state. This is possible if there is no unpaired carriers in the superconductor, which always compensate for the inhomogeneous charge distribution of Cooper pairs in metallic superconductors in the course of superconducting current flow. Calculations performed by Gufan et al.[18] showed that at $I = 0.1$ A at 4.2 K in the surface layer of $\sim 10^{-7}$ cm an electric field of ~ 1 kV / cm may appear at the film thickness below 10^{-4} cm and Cooper pair density less than 10^{17} cm^{-3}. Such a field can destabilize a loose structure of (123) and explain the observed effects.

From paper[19] it follows that in general the growing temperature of the superconducting transition leads to smaller structural stability.

9. CONCLUSION

The experimental results recently obtained while studying the YBCO, Bi (2223) structural instability at the current flowing at helium, nitrogen, and room temperatures show that there exists a phenomenon that, in case it is not overcome, may cause principle limitations for the possible applications of this class of substances in practice. If our first results obtained at polycrystalline samples were regarded with criticism, now the analogous effects are observed at quasi – single – crystal films with the c – axis perpendicular to the film surface and a high critical current.

Despite the fact that the crystalline structure of the cuprate HTCS, as it was noted in one of the previous papers, is favorable for the transfer of certain ions, the problem of the direct connection of the superconductivity phenomenon with the crystalline instability is still unsolved.

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