POSSIBLE COMPOSITION CHANGES OF THE $YBa_2Cu_3O_x$ SURFACE LAYER ON THE BOUNDARY WITH NEGATIVE CHARGE

GERMAN MOISEEV[1], JAROSLAV ŠESTÁK[2]* AND BEDŘICH ŠTĚPÁNEK[2]

[1] *Institute of Metallurgy, Russian Academy of Science, Ural Division, Ekaterinburg, 620219, GSP-812, Amundsen, 101, Russian Federation*

[2] *Institute of Physics, Department of Semiconductors, Academy of Sciences of the Czech Republic, Cukrovarnická 10, 162 00 Praque – 6, Czech Republic*

Received 8. 6. 1994

Ideal ($x = 7$) and close to real ($x = 6.85$) composition of the $YBa_2Cu_3O_x$ superconductor can be assumed to change on the boundary with negative charge surface. The two used methods of calculation (generalized measurements and absorption) show a considerable reduction of copper ion valence.

INTRODUCTION

When the crystal lattice is contacted against a negative charged surface it is necessary to take into account boundary effect and corresponding changes created in the interface layer on the boundary. In particular this concept was applied for the investigation of ionic melts but so far there was no such an attempt paid to the oxide high T_c superconductors (HTSC). Although hypothetical, we tried to evaluate such a situation under two different assumptions: (i) absorption [1] and (ii) generalized moments [2] of ions. It was applied for the $YBa_2Cu_3O_x$ type superconductor assuming ideal ($x = 7$) and close to real ($x = 6.85$) compositions. According to the electroneutrality they can be represented as follows:

$$A \; ..... \; Y_1^{3+}BA_2^{2+}Cu_2^{2+}Cu_1^{3+}O_7^{2-}$$

$$B \; ..... \; Y_1^{3+}Ba_2^{2+}Cu_{2.6}^{2+}\,Cu_{0.4}^{3+}\,\square_{0.15}^{2+}\,O_{6.85}^{2-} \qquad (1)$$

taking in account the possible coexistence of trivalent copper and holes (□) with the positive charge of two. The aim of present work is to investigate possibilities for a composition change as the response for the excess of negative charge along the contacting surface.

METHODS

Let us assume that the electron flow creates negative charge on the surface of HTSC. In response it can cause absorption and/or transport of positively charged ions into the HTSC surface or the desorption of negative ions. It can be analyzed in two ways:

2.1. Probability method

For a generalized moment of i-th ion it is valid that $m_i = z_i/r_i$, where z_i and r_i are the charge and radious of ion respectively. For positive ions (or holes) the relative ability for the absorption (C_i) is inversely proportional to generalized moment, or

$$C_i = 1/m_i = r_i/z_i \qquad (2)$$

on contrary, for negative ions, it represents the ability for desorption [2]. In table I. there are given values of m_i and C_i for ions in the formula group of Eq. (2). Ions radii were compiled from ref. [4] taking in account their coordination number in HTSC-structure. The hole radius was considered equal to that of O^{2-}. From table I it follows that the absorption ability of positive ions decreases in the row $Ba^{2+} \rightarrow \square^{2+} \rightarrow Y^{3+} \rightarrow Cu^{2+} \rightarrow Cu^{3+}$. The most realiable seems be the transition of Ba ion into the surface layer while the lowest chance exhibits Cu^{3+}.

The general probability of absorption/desorption for some ions (hole) into surface layer ($\sum W_i$) is assumed equal 1. If only one ion is absorbed then $\sum W = W_i = 1$. If absorption of several ions take place each of them has a part of the total probability (< 1). Consequently $W_i = C_i/\sum C_i$ (where $\sum W_i = 1$) and the values C_i and W_i can be read from Table I.

Considering the absorption of each cation (Γ_i) proportional to W_i and number of ions of the same kind n_i^a) in formula group (1):

$$\Gamma_i = n_i^a . W_i \qquad (3)$$

Then in surface layer will be the following number of ions of each kind

$$\bar{n}_i^{(s)} = n_i^a + \Gamma_i = n_i^a(1 + W_i) \qquad (4)$$

Here we supposed, that the relative area occupied by a molecule of HTSC in the bulk and on the surface

---

*Correspondece to: Prof. J. Sestak, Institute of Physics, Department of Semiconductors, Academy of Sciences of the Czech Republic, Cukrovarnická 10, 162 00 Prague – 6, Czech Republic

Table I.

Generalized moments of ions, their ability to absorption/desorption and the values of C_i and W_i ions for HTSC.

ion	$r \times 10^{10}$ [m]	$m \times 10^{10}$ [C.m^{-1}]	$YBa_2Cu_3O_7$		$YBa_2Cu_3O_{6.850.15}$	
			$C_i \times 10^{10}$ [m.C^{-1}]	W_i	$C_i \times 10^{10}$ [m.C^{-1}]	W_i
Y^{3+}	1.02	2.94	0.34	0.151	0.34	0.115
Ba^{2+}	1.47	1.36	0.735	0.327	0.735	0.25
Cu^{2+}	0.57	3.318	0.301	0.134	0.301	0.102
Cu^{3+}	~(0.54)	5.56	0.18	0.080	0.18	0.061
O^{2-}	1.38	-1.45	-0.69	0.307	-0.69	0.235
$\square^{2+}$	~(1.38)	1.45	–	–	0.69	0.235

Table II.

Ions content in 1 cm^2 of surface of HTSC without regard to absorption.

	$YBa_2Cu_3O_7$		$YBa_2Cu_3O_{6.85}\square_{0.15}$	
ion	n_i^0 in molecule	$n_i^{(s)} \times 10^{-14}$ [ion.cm^{-2}]	n_i^0 in molecule	$n_i^{(s)} \times 10^{-14}$ [ion.cm^{-2}]
Y^{3+}	1	3.218	1	3.218
Ba^{2+}	2	6.436	2	6.436
Cu^{2+}	2	6.436	2.6	8.359
Cu^{3+}	1	3.218	0.4	1.286
O^{2-}	7	22.526	6.85	22.023
$\square^{2+}$	–	–	0.15	0.482
		$\sum = 41.795$		$\sum = 41.795$

before and after the absorption will be the some and constant because the electroneutrality is maintained in the surface monomolecular layer.

There are two ways of how to treat a negative ion (O^{2-}). First, we can assume a "vector" absorption where absorption of positive ions has the sign "plus" and that of negative ones has the sign "minus". Second from the surface layer "leaves" a number of O^{2-} ions equal to the sum of all cations absorbed into the layer, i.e. oxygen anions are displaced, i.e.

$$\Gamma_{O^{2-}} = \sum \Gamma_{i_{cations}} .$$

In common, we can analyze both of them following the schemes:

1/ "vector" absorption of all ions (1A an 1B),

2/ absorption of all positive ions with displacement of equivalent number of O^{2-} into the HTSC bulk (2A and 2B),

3/ absorption Ba^{2+} and $^{2+}$ with displacement of O^{2-} into the bulk (3B),

4/ absorption only Ba^{2+} with displacement of O^{2-} into the bulk (4A and 4B).

In order to exemplify the calculation the simplest treatment is given below for the scheme 4A. Absorption of only Ba^{2+} is considered with the displacement of O^{2-} for the initial composition $YBa_2Cu_3O_7$. If only one ion is accounted for, then

$$W_{Ba^{2+}} = 1 \text{ and } \Gamma_{Ba^{2+}} = 2,\ n^{(s)}_{Ba^{2+}} = 4,\ n^{(s)}_{O^{2-}} = 5;$$

yielding the surface layer composition

Table IIIa.

Results of evaluation of surface layer composition by probability method (I).

Kind of ions	Treatment variation	For initial $YBa_2Cu_3O_x$							
		Y^{3+}	Ba^{2+}	Ba^0	Cu^{3+}	Cu^{2+}	Cu^0	$\square^{2+}$	O^{2-}
"Vector" absorption 1A all ions	1st	1	2.306	0	0	0	0.438	0	4.463
	2nd	1	2.306	0	0.438	0	2.37	0	4.463
Absorption accordingly to $\Gamma_0^{2-} = -\sum \Gamma_i$ cations 2A all ions	1st and 2nd	1	2.306	0	0.85	0	2.06	0	5.081
3A	1st and 2nd	The same as 4A							
4A just for Ba^{2+}	1st and 2nd	1	3.5	0.5	0	0	3	0	5

$Y^{2+}Ba_4^{2+}Cu_2^{2+}Cu^{3+}O_5^{2-}$ where the sum of the positive charges is 18 and that of the negative ones is 10. Excess of positive charges can be neutralized by negative charges of electron flow. Consequently the two valence Cu and than the three valence Cu-ions are reduced and finally ions Ba^{2+} and Y^{3+}, thus first 7 from 8 positive excessive charges can be neutralized $2Cu^{2+} + Cu^{3+} + 7e = 3Cu^0$ and the rest positive charge can be compensated by $0.5Ba^{2+} + e = 0.5Ba^0$. After this procedure and when accounting for the electroneutrality, the composition of the surface layer is $Y^{3+}Ba_{0.5}^{3+}Ba_{3.5}^{0}Cu_3^0O_5^{2-}$ or $Y^{3+}Ba_{3.5}^{2+}O_5^{2-}$ together with $Ba_{0.5}Cu_3$.

2.2. Method by Moiseev and Stepanov [5].

In 1 cm^3 of HTSC-volume the number of molecules (Π) is $\Pi = (dN_0)/m$, where d is the density, M is the molecual mass and N_0 is the Avogadro number. Here we supposed that the molecules are uniformly distributed in one cubic cm, thus, $\Pi = n^3$, where n is the number of molecules in the tube side with length 1 cm. In the layer with the thickness equal to the average size of molecule and area 1 cm^2 there are following number of molecules

$$n^{(s)} = n^2 = \left((d.N_0)/M\right)^{2/3} \tag{5}$$

where $n^{(s)}$ is the number of molecules in the initial composition on the area 1 cm^2 without absorption.

The total number of ions on this area is:

$$\sum n_i^{(s)} = n^{(s)} \sum n_i^a, \tag{6}$$

where $n_i^{(s)}$ is the number of ions of each kind in 1 cm^2 area, n_i^a is the number of ions of each kind in the formula group (1). The number of ions of each kind in 1 cm^2 area would then equal

$$n_i^{(s)} = n^{(s)} n_i^a = n_i^a \left((d.N_0)/m\right)^{2/3}. \tag{7}$$

In Table II. there are given contents of each kind of ions in 1 cm^2 area of monomolecular layer without regard to absorption if

$d_{(YBa_2Cu_3O_x)}$

equals to 6.38 g/cm^3 [6]; $M = 666.18$ and $N_0 = 6.023 \times 10^{23}$. Absorption of i-th cation is $\Gamma_i = \bar{W}_i \Gamma_{ab}$, where Γ_{ab} is common absorption all cations in surface layer, ions/cm^2 and $\bar{W}_i$ is the probability of cation absorption, normalized to 1. Then

$$\bar{W}_i = C_i n_i^{(s)} / sum\left(C_i n_i^{(s)}\right), \tag{8}$$

where C_i is the ability of cations absorption (see Table I.), $n_i^{(s)}$ is the number of ions of each kind in 1 cm^2 area without regarding the absorption (ct. Table II.). The content of i-cation in surface layer after absorption $\bar{n}_i^{(s)}$ can be found as a sum

$$\bar{n}_i^{(s)} = n_i^{(s)} + \Gamma_i = n_i^{(s)} + \bar{W}_i.\Gamma_{ab}. \tag{9}$$

Table IIIb.

Results of evaluation of surface layer composition by probability method (I).

Kind of ions	Treatment variation	For initial $YBa_2Cu_3O_{6.85}\,\square_{0.15}$							
		Y^{3+}	Ba^{2+}	Ba^0	Cu^{3+}	Cu^{2+}	Cu^0	$\square^{2+}$	O^{2-}
"Vector" absorption 1A' all ions	1st and 2nd	1	2.242	0	0.38	0.252	2.384	0.166	4.73
Absorption accordingly to $\Gamma_0^{2-} = -\sum \Gamma_i$ cations 2A' all ions	1st and 2nd	1	2.3	0	0.375	0.357	2.196	0.17	4.89
3A'	1st and 2nd	1	3.03	0	0.4	0.391	2.209	0.233	5.744
4A' just for Ba^{2+}	1st and 2nd	1	3.2	0.8	0	0	3	0.15	4.85

The contents of O^{2-} ions in surface layer regarding the absorption [5] is

$$\bar{n}^{(s)} = n^{(s)}_{O^{2-}} - \sum \bar{n}^{(s)}_i .$$

In order to calculate the composition it is necessary to know the value Γ_{ab} for which we used 3.75×10^{14} ions/cm^2. It was deduced on bases for common absorption Na^+ and K^+ ions as received from experimental data for the surface tension in Na_2CO_3 and K_2CO_3 melts [5]. The generalized moment of K^+ and Na^+ equal to 1.2×10^{-10} and 1.63×10^{-10} C/m, moments of Ba^{2+} and $\square^{2+}$ equal 1.36×10^{-10} and 1.46×10^{-10} C/m), respectively. The procedure for neutralization of the excessive positive charges of ions was the same as above.

RESULTS

The composition of surface layers regarding the absorption calculated by two methods are given in Table III. Analysis shows that the best agreement is observed for schemes 2A and 2A', 3B and 3B' (ct. Table IV.).

We can suppose that the agreement of results by using the independent methods of calculations serve as a criterion of the reliability for this results. On this ground we supposed that the compositions of surface layers calculated by the schemes 2A and 2A', 3B and 3B' are the most representative from all results. Consequently, the most probable way of change of the surface compositions is the absorption (or transfer) of ions Ba^{2+} and $\square^{2+}$ from the bulk of HTSC. This has a good agreement with a maximum of absorption ability for Ba^{2+} and $\square^{2+}$ in comparison with the other ions (Table I.).

For selected compositions the concentration of ions Ba^{2+} and $\square^{2+}$ increase approximately by 1.5 times while ions O^2 are approximately 1.2 times less as well as the sum of ions Cu^{2+} and Cu^{3+} in comparison with that in the volume HTSC. That surface HTSC layer can be described in common by formulae:

$$Y^{3+}Ba^{2+}_{2.77-2.306}Cu^{3+}_{0.22-0.85}O^{2-}_{4.6-5.08}$$

(schemes 2A and 2A')

and

$$Y^{3+}Ba^{2+}_{3.03-3.09}Cu^{2+}_{0.392-0.26}Cu^{3+}_{0.4}O^{2-}_{5.744-5.677}\,\square^{2+}_{0.223-0.226}$$

(schemes 3B and 3B'),

which brings necessity to introduce atoms of metallic copper.

DISCUSSION

The above results are evidently dependent on certain hypothetical assumptions and their approval would need a serious "energetic" test of possibility

Table IIIc.

Results of evaluation of surface layer composition by method [5] (II).

Kind of ions	Treatment variation	For initial $YBa_2Cu_3O_x$							
		Y^{3+}	Ba^{2+}	Ba^0	Cu^{3+}	Cu^{2+}	Cu^0	$\square^{2+}$	O^{2-}
"Vector" absorption 1A all ions	1st	1	0.843	1.448	0	0	2.256	0	2.343
	2nd	1	2.77	1.448	0.22	0	3.256	0	4.6
Absorption accordingly to $\Gamma_0^{2-} = -\sum \Gamma_i$ cations 2A all ions	1st and 2nd	1	2.77	0	0.22	0	2.903	0	4.6
3A	1st and 2nd	The same as 4A							
4A just for Ba^{2+}	1st and 2nd	1	3.175	0	0.794	0	2.206	0	5.866

of ion transport. In addition, there is a difficult comparison between melts (at 900°C [5]) and the HTSC at liquid nitrogen (almost 70 K), where the movement of ions can exhibit considerable difficulties. If assuming that electron (or holes) flow does produce negative charges worth of consideration it can definitely allow us to imagine not only the polarization of ions in the HTSC structures but also the initiation of the transport of positive ions into the negative charged surface.

It is expedient to evaluate energies of this transport by carrying out special investigations. In this work we supposed a priori that the possiblity of transport of positive ions into crystal surface layer could be taken comparable to a spontaneous absorption of surface-active substances in melts of alkali-metals carbonates at higher temperatures which does not generally contradict the laws of physical chemistry. Our previous thermodynamic treatments [7,8] showed possibility for warying the compositions in a wide spectrum and stability.

Few experimental data so far published support principally our results. It was shown [9] that there are definite composition changes nearby the positive electrode (negative polarity field) when a constant current is passing through the HTSC-film at 4.2 K during several days. By comparing with the positive field the content of copper was found to increase by 4 wt. %. Some inclusions were found to have the content of copper as high as 38 wt.% [9]. For similar investigations, carried out at 300 K, new phases were observed to be created nearby the positive electrode (Y_2BaCuO_x, $BaCuO_z$, CuO_δ and tetragonal $YBa_2Cu_3O_Y$), as well as the enrichment of copper content [10]. The changes of HTSC-composition, however, were not experimentally observed in the fields with positive polarities [9, 10]. Consequently, the transfer of positive ions of copper from the bulk of HTSC to the negative charged surfaces, their reduction up to metallic state, and the change of HTSC composition can be assumed plausible [9, 10], but the mechanism of such a transfer is not clear yet.

In the framework of our models we did not take into account the existence of Cu^{+1} in the HTSC-surface layers as this assumption would break the law of electroneutrality in monomolecular surface layer of the given HTSC-compositions, see eq. 1. Nevertheless, it is possible to estimate average charge of copper atoms taking into account the sum of all ions charges and the total number of ions and neutral atoms of copper in the surface layer (see eq. 1 and Table IV). After calculations the following charge values per 1 atom of copper in the surface layer are received:

variant	average charge
2A (I)	+ 0.68
2A'(II)	+ 0.28
3 B (I)	+ 0.66
3B' (II)	+ 0.59

Table IIId.

Results of evaluation of surface layer composition by method [5] (II).

Kind of ions	Treatment variation	For initial $YBa_2Cu_3O_{6.85}\,\square_{0.15}$							
		Y^{3+}	Ba^{2+}	Ba^0	Cu^{3+}	Cu^{2+}	Cu^0	$\square^{2+}$	O^{2-}
"Vector" absorption 1A' all ions	1st and 2nd	1	1.114	1 153	0	0	3.151	0.146	2.614
Absorption accordingly to $\Gamma_0^{2-} = -\sum \Gamma_i$ cations 2A' all ions	1st and 2nd	1	2.6	0	0.325	0	3.015	0.14	4.727
3A'	1st	1	3.091	0	0.4	0.26	2.338	0.226	5.677
	2nd	1	3.091	0	0.4	0.26	2.126	0.226	5.677
4A' just for Ba^{2+}	1st and 2nd	1	3.062	0	0.4	0.472	2.126	0.15	5.782

Taking into account the date of Table IV, we can give the integral compositions of surface HTSC-layers in the following stoichiometry: variants 2A(I) and 2A' (II)

$$Y^{3+}Ba^{2+}_{2.307-2.77}Cu^{(0.68+)-(0.29+)}_{3.753-2.28}O^{2-}_{5.08-4.6}$$

and variants 3B (I) and 3B' (II)

$$Y^{3+}Ba^{2+}_{2.306-2.77}Cu^{0.661+)-(0.594+)}_{3-2.898}O^{2-}_{5.744-5.667}\,\square^{2+}_{0.223-0.226}.$$

Table IV.

Compare of compositions of surface layer by two independent methods

Ions and metals in composition	Coefficient of ions and metals			
	Scheme and method		Scheme and method	
	2A(I)	2A'(II)	3B(I)	3B'(II)
Y^{3+}	1	1	1	1
Bu^{2+}	2.306	2.77	3.03	3.091
Cu^{2+}	–	–	0.391	0.26
Cu^{3+}	0.85	0.22	0.4	0.4
O^{2-}	5.08	4.6	5.744	5.677
$\square^{2+}$	–	–	0.223	0.226
Cu^0	2.903	2.06	2.209	2.238

Furthermore, in our proposed model we did not attempt to discuss aditional possibilities of chemical interactions between the surface layers and bulk HTSC-compositions. This problem will be the subject of our further investigations, but we can anticipate that such chemical reactions can lead to a formation of new phases as we already suggested in our simulated thermodynamics calculations of thermochemical properties of real and hypothetical phases auxiliary to the YBaCuO HTSC [8].

References

[1] D. W. Gibbs, Thermodynamical works, (Russian Translation) Moscow (1950).

[2] W. K. Semenchenko, *Surface phenomena in metals and alloys*, Moscow (1957).

[3] G. K. Moiseev and G. K. Stepanov, Reports of Institute Electro-chemistry, Ural Branch Academy of Science USSR *5*, 105 (1964).

[4] S. S. Batsanov, J. Inorg. Chem., USSR, ***36***, 3015 (1991).

[5] G. K. Moiseev and G. K. Stepanov, J. Phys. Chem., USSR *40* 61 (1966).

[6] I. H. Park, P. Kostic and I. R. Singh: Mater. Letters *6*, 393 (1988).

[7] G. K. Moiseev, S. I. Zeitzeva, N. A. Vatolin and J. Šesták, Thermochim. Acta *216*, 301 (1993).

[8] J. Šesták, G. K. Moiseev and I. Tsagareisvili, J. Jap. Appl. Phys.: *33*, 97 (1994).

[9] A. M. Prochorov, Ju. M. Gufan, A. E. Krapivka, E. H. Lubnin, G. N. Michailova, E. G. Rudashevski, A. S. Seferov, V. N. Sumarokov, V. A. Tarasenkov, and A. G. Thistov: Letters to J. Exper. and Theoret. Phys. USSR *51*, 132 (1990).

[10] V. N. Sumarokov, V. A. Tarasenkov, A. G. Thistov, Ju. M. Gufan, A. E. Krapivka, E. H. Lubnin, G. N. Michailova, A. M. Prochorov, E. G. Rudashevski and A. S. Seferov: Superconductivity: physics, chemistry, technology USSR, *3* 2081 (1990).

Submitted in English by the authors

ZMĚNY SLOŽENÍ V POVRCHOVÉ VRSTVĚ SUPRAVODIČE $YBa_2Cu_3O_x$ VYVOLANÉ KONTAKTEM SE ZÁPORNÝM NÁBOJEM

German Moiseev[1], Jaroslav Šesták[2] a Bedřich Štěpánek[2]

[1] *Ustav metalurgie, Uralská sekce Ruské Akademie Věd, GSP-812, Amundsena 101, Ekatěrinburg, 620219 Rusko*
[2] *Oddělení polovodičů, Fyzikální ústav Akademie věd České republiky, Cukrovarnická 10, CZ - 162 00 Praha 6*

Ideální (X=7) a reálné (X=6.85) složení vysokoteplotního keramického supravodiče ($YBa_2Cu_3O_x$)bylo analyzováno v podmínkách povrchového kontaktu s negativním nábojem při použití dvou výpočetních metod, tj. pravděpodobnostního odhadu, na základě zobecněných momentů zůčastněných iontů a způsobu navrženém Moiseevem a Stěpanovem, na základě adsorbce iontů. Ukazuje se, že v přítomnosti záporného náboje může hypoteticky dojít v povrchové vrstvě supravodiče k podstatné redukci kationtů mědi a to v rozsahu valence (0.28–0.68)+, uvažujeme-li průměrnou sumární hodnotu náboje kationtů a neutrálních atomů mědi ()+ existujících v souladu s výpočetními metodami v analyzované kontaktní vrstvě. Předpokládaná změny stechiometrie je pak následující:

Ideální složení $Y^{3+}Ba_2^{2+}Cu_2^{2+}Cu^{3+}O_7^{2-}$ se posune na

$$Y^{3+}Ba^{2+}_{2.307-2.77}Cu^{(0.68+)-(0.29+)}_{3.753-2.28}O^{2-}_{5.08-4.6}$$

a reálné $Y^{3+}Ba_2^{2+}Cu_{2.6}^{3+}\square_{0.15}^{2+}O_{6.85}^{2-}$ na

$$Y^{3+}Ba^{2+}_{2.306-2.77}Cu^{0.661+)-(0.594+)}_{3-2.898}O^{2-}_{5.744-5.667}\square^{2+}_{0.223-0.226}.$$

(kde □ označuje díry).