INFLUENCE OF CALCIUM ON TRANSPORT PROPERTIES, BAND SPECTRUM AND SUPERCONDUCTIVITY OF $YBa_2Cu_3O_y$ AND $YBa_{1.5}La_{0.5}Cu_3O_y$.

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The comparative investigation of transport phenomena in $Y_{1-x}Ca_xBa_2Cu_3O_y$ (0<x<0.25, 6.96>y>6.87 and 6.73<y<6.53), $Y_{1-x}Ca_xBa_{1.5}La_{0.5}Cu_3O_y$ (0<x<0.5, 7.12>y>6.96) and $YBa_{2-x}La_xCu_3O_y$ (0<x<0.5, 6.95<y<7.21) systems have been carried out. The temperature dependencies of resistivity and thermopower have been measured. It was found that the S(T) dependencies take some additional features with Ca content increase. The results obtained have been analyzed on the basis of the phenomenological theory of electron transport in the case of the narrow conductive band. The main parameters of the band spectrum (the band filling with electrons degree and the total effective band width) have been determined. The dependencies of these ones from contents of substituting elements are discussed. Analyzing the results obtained simultaneously with the tendencies in oxygen content and critical temperature change we have confirmed the conclusion that the oxygen sublattice disordering has a determinant effect on band structure parameters and superconductive properties of $YBa_2Cu_3O_y$. The results obtained suggest that Ca gives rise to some peculiarities in band spectrum of this compound.

1. INTRODUCTION

An important question arising in studies of HTSC-materials is the elucidation of role and mechanism of influence of different structural elements of unit cell on superconductivity and other properties of these compounds. Influence of non-isovalent substitutions on different properties of $YBa_2Cu_3O_y$ are discussed in many papers. The common property of these substitution (in parallel with critical temperature T_c depression) is influence on oxygen content and oxygen sublattice condition as a whole. The calcium holds a distinctive position amount the substituting elements. Whereas other elements increase leads to increase of y value (Fe,Co,Al in place of Cu [1-3], La in place of Ba [4-5]), introduction of Ca decreases the one [6-7]. This tendency retains for additional substitution for Y by Ca in Y-Ba-Cu-O system with different dopants (Co→Cu [8], Al→Cu [9], La→ Ba [10]). Furthermore, in these cases the T_c value increases when compared with single substitution samples. However, the questions of band spectrum structure, of its parameters dependence on the samples composition and of connection of these parameters values with superconductive properties are still the open questions. One way to obtain samples with trended composition change. The analysis of transport phenomena in $YBa_2Cu_3O_y$ on the basis of our phenomenological theory [11] has permitted not only to account for all the specific features of temperature and concentration dependencies of transport coefficients but also to describe quantitatively their behavior as well as to determine the conductive band parameters values. As a result, we were able to follow the band spectrum transformation with oxygen content change in $YBa_2Cu_3O_y$ [11] and with iso- and non-isovalent substitution for different components of unit cell of this HTSC and to observe the correlation between band spectrum change and T_c value change [12-13]. In this paper we use our model for investigation of Ca influence on transport properties in normal phase and band spectrum transformation character in the system Y-Ba-Cu-O.

2. SAMPLES AND EXPERIMENT DETAILS

The ceramic samples investigated were prepared from high purity Y, La and Cu oxides and Ba and Ca carbonates by standard solid-state reaction for the $YBa_2Cu_3O_y$ compounds. The pellets were annealed in air three times with intermediate regrinding at temperature T=920-950°C. Then the samples were cooled slowly and were annealed in flowing oxygen at T=450°C, attended slow cooling to room temperature. Lowering of the oxygen content in the samples $Y_{1-x}Ca_xBa_2Cu_3O_y$ was achieved by annealing at T=450°C that was followed by quenching to room temperature. The oxygen content was determined by the iodometric titration method accurate to ±0.01-0.02. The X-ray analysis has revealed all the samples studied to be single phase.

The temperature dependencies of the resistivity, ρ(T), and that of the thermopower, S(T), were measured over the temperature range $T=T_c$-300K. The resistivity was measured by the standart ac four probe method with frequency and phase selection of the measurement channel. The absolute value of thermopower was determined with respect to copper electrodes and then corrected for the absolute value of the thermopower of copper. The temperature difference during the S measurements was 1-2K and was measured with a differential copper-constantan thermocouple.

3. RESULTS AND DISCUSSION

The values of oxygen content, the superconducting transition parameters and the values of thermopower at T=300K for all the samples investigated are shown in Tables 1-3. First of all, we discuss results for series 1 and 2 with single substitution. The behavior of ρ and S in normal phase has certain specific features already described in literature. The dependence ρ(T) is linear within a wide temperature range. The main features of thermopower are the weak dependencies S(T) within the wide temperature range and the smooth maximum of S(T) observed at low temperatures. However, the influence of dopant content increase on S(T) transformation is different for Ca and La. The value of S is practical constant with Ca content increase, whereas La increasing leads to significant growth of thermopower. In both cases the maximum of S(T) is shifted to higher temperatures with x (see. Fig.1, Fig.2). The T_c value decreases with dopant content increase in both series (see Table 1).

Table 1.
The oxygen content, parameters of superconductive transition and thermopower in single-substiturted samples.

x	y	T_c^m, K	T_c^o, K	S(300K), μV/K
		$Y_{1-x}Ca_xBa_2Cu_3O_y$		
0.000	6.96	92.3	90.7	-0.63
0.025	6.95	91.5	86.8	-1.48
0.050	6.93	88.2	83.3	-1.18
0.100	6.91	83.3	71.9	-1.14
0.150	6.90	79.0	71.5	-1.29
0.200	6.89	78.2	66.6	-1.24
		$YBa_{2-x}La_xCu_3O_y$		
0.00	6.95	88.2	85.4	0.78
0.05	6.98	89.8	88.8	1.12
0.10	6.99	90.2	89.5	6.32
0.20	7.03	91.5	86.9	7.67
0.30	7.10	84.2	76.8	16.63
0.40	7.14	73.3	64.2	26.35
0.50	7.21	55.7	49.7	33.98

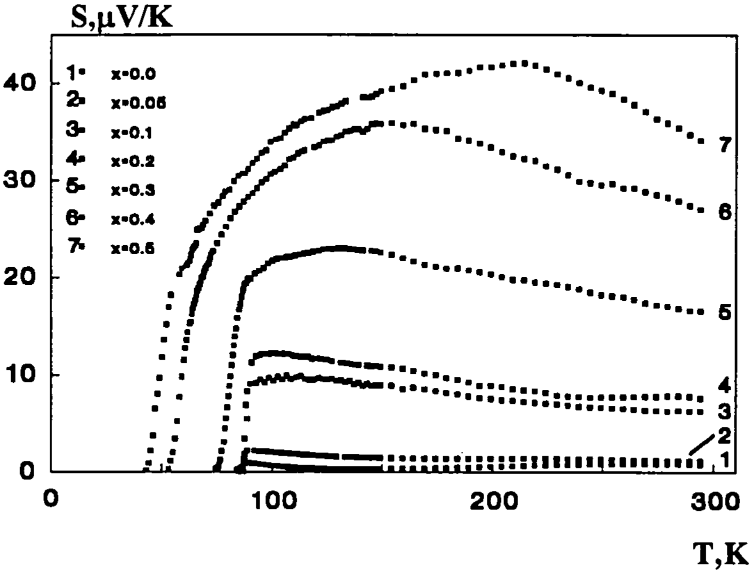

Fig.1. The thermopower vs. temperature for $YBa_{2-x}La_xCu_3O_y$.

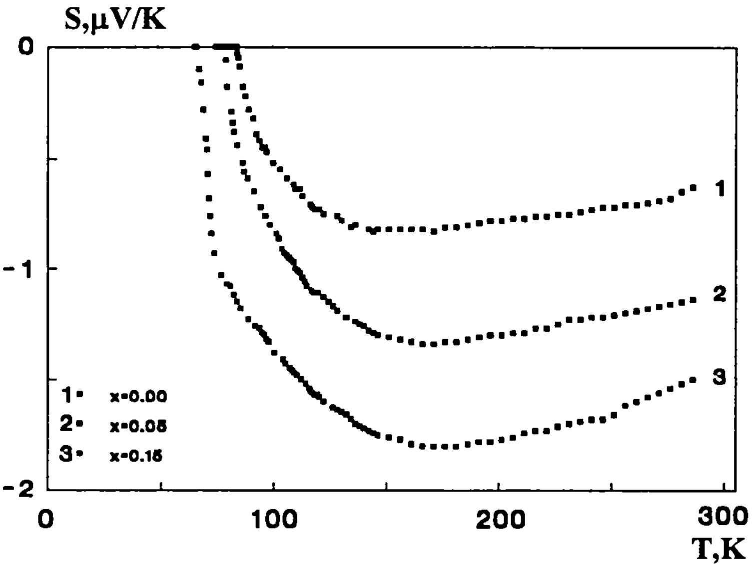

Fig.2. The thermopower vs. temperature for $Y_{1-x}Ca_xBa_2Cu_3O_y$

The results obtained have been analyzed on the basis of narrow-band model. This model assumes the transfer of charge carriers along the band whose width is much less than in usual metals or semiconductors (comparable to the k_oT value). The charge carries concentration is believed to remain constant with temperature change and is determined by the band filling degree with electrons F. This paramėter is equal to the ratio of the numbers of electrons to the numbers of states in the band. The F value determines the value and the sign of the thermopower in the region of high temperatures whenS=const(T) according with the formula:

$$S = \frac{k_o}{e} \cdot \ln \frac{F}{1-F}, \tag{1}$$

Thus, changes of F (and correspondingly, S(300K)) occurring with the deviations from the $YBa_2Cu_3O_y$ stoichiometric content (oxygen deficit increase, doping with various elements) results in changing of the conduction band parameters and the number of carriers in the band. In Ref. [11] we have shown that for describing temperature dependencies in the whole temperature range we can use the simplest approximation of density of states D(E) and differential conductivity σ(E) functions as rectangles with different widths. In this case we can obtain the analytic expressions for temperature dependencies of the transport coefficients. As this take place, contrary to resistivity and Hall coefficient the thermopower may be calculated to absolute value:

$$S = -\frac{k_o}{e}\cdot\left\{\frac{W_\sigma^*}{\mathrm{sh}W_\sigma^*}\cdot\left[e^{-\mu^*} + \mathrm{ch}W_\sigma^* - 1/W_\sigma^*\cdot\left(\mathrm{ch}\mu^* + \mathrm{ch}W_\sigma^*\right)\cdot\ln\frac{e^{\mu^*}+e^{W_\sigma^*}}{e^{\mu^*}+e^{-W_\sigma^*}}\right] - \mu^*\right\}, \qquad (2)$$

where: $\mu^* \equiv \mu / k_o T = \ln\frac{\mathrm{sh}(F\cdot W_D^*)}{\mathrm{sh}\left((1-F)\cdot W_D^*\right)}$,

μ is the chemical potential, $W_D^* \equiv W_D/2k_oT$, $W_\sigma^* \equiv W_\sigma/2k_oT$, W_D is the total effective band width (the width of D(E) rectangle) and W_σ is effective width of the conductive states interval (the width of σ(E) rectangle).

The W_σ and W_D values are different. This may be due to a different nature of energy dependencies of the density of states (DOS) and the differential conductivity functions, as well as to the probable localization of the states near the band edge caused by a disordering in the lattice. In the case of $YBa_2Cu_3O_y$ with y=7 the Fermi level E_F is situated in the middle of the band near the maximum of the DOS function. In this case F=0.5 and energy parameters of the band W_D=70-90meV and W_σ=30-40meV [11]. With the oxygen content y decreasing the number of charge carriers (holes) decreases (the F value increases) which leads to the E_F displacement from the middle of the band (the DOS function maximum) to its upper edge. Also, the oxygen deficit increase is accompanied by the increase of the oxygen vacancy disordering in the lattice. According to Anderson's theory [14], this leads to the localized states share increase (in our model this corresponds to the W_σ/W_D-ratio decrease). The total band width increases in this case which causes the general drop of the DOS including $D(E_F)$. As result of this the T_c value decreases.

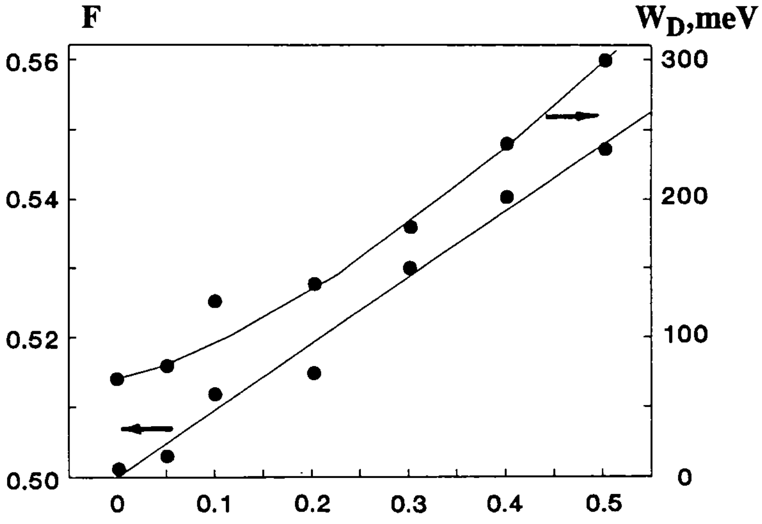

Fig.3. The band parameters vs. La content in $YBa_{2-x}La_xCu_3O_y$

Preparatory to discuss the results obtained on the basis of the model described above, one remark needs to be made. If the band filling is closed to half, the details of the band spectrum structure could influence the S(T) dependencies significantly, i.e. the approximation used becomes rough. In this reason we haven't calculated the band structure parameters for Ca-doped samples in which the

S(300K) value is closed to zero and thus F≈0.5. In this case we can make only the qualitative conclusion that the F value is practical constant and the W_D value increases with x. As to the La-doped samples (in which S(300K) value increases significantly with x) the calculated values of the main band spectrum parameters are shown in Fig.3. It can be seen that the La content increase leads to appreciable transformation of the conductive band.

The results obtained for both series with single substitution may be explained with regard to the oxygen sublattice condition change. The La^{3+} ions substitute for Ba^{2+} causing O(5) sites to become filled with oxygen in so doing the oxygen comes from both atmosphere during annealing and from neighboring cells without La. As a result, the oxygen deficiency arises in cells which don't contain La atoms. In additional, the total compensation of the excess positive charge don't take place, as result the electrons number increases (in our terms, the F value increases). In the case of Ca-doping the oxygen content decreases with x, but because Ca^{2+} ions substitute Y^{3+} increasing the holes number in the band, the increase of electrons at the expense of oxygen deficit increase is compensated. As a result the F value remains constant with Ca content increase. Thus, broadening of the band in both cases is caused by increasing of oxygen sublattice disordering degree and leads to T_c suppression. Difference of the F(x) dependencies are explained by different relationship between valences of substituting elements and substituted ones.

Table 2.
The oxygen content, parameters of superconductive transition and thermopower in $Y_{1-x}Ca_xBa_{1.5}La_{0.5}Cu_3O_y$.

x	y	T_c^m, K	T_c^o, K	S(300K), μV/K
0.0	7.22	36.6	32.0	40.49
0.1	7.19	57.9	51.7	18.98
0.2	7.13	73.0	67.9	19.19
0.3	7.08	80.6	78.9	3.34
0.4	7.01	82.4	80.2	6.19
0.5	6.96	82.5	78.9	4.23

By virtue of the fact that Ca and La influence differently on oxygen content, the investigation of the properties of the samples with double substitutions has been of our interest. It is of significance to study the transport properties of $Y_{1-x}Ca_xBa_{2-z}La_zCu_3O_y$ and to follow the band structure transformation in the case of additional substitution for Y by Ca with z value fixed when comparing with single substitution (for Ba by La) system. In this case the y value decreases with x as with single-doping by Ca samples (see Table 2). The temperature dependencies of resistivity and thermopower are shown in Fig.4 and Fig.5, the parameters of superconductive transition are given in Table 2. The Ca increase leads to decreasing of S(300K) value and increasing of the critical temperature accompanied by narrowing of superconductive transition and increasing of the slope of ρ(T) dependencies. The ρ(T) dependencies are linear except the start sample with x=0.

The following fact has engaged our attention. Whereas the ρ(T) dependencies are similar to the typical ones for Y-Ba-Cu-O system, the dependencies S(T) are modified with Ca content not quite usually. As known for the dependencies S(T) in $YBa_2Cu_3O_y$ with various oxygen content or different cations substitutions, the slope of S(T) gradually decreases with temperature in the region above S(T) maximum. In case of slight variations from stoichiometry the value of S is almost constant at the temperature range near T=300K. As illustrated in Fig.5, in the samples doped with Ca the conservation of well-pronounced maximum is accompanied by showing up of region of linear S decreasing with T above the temperature of this maximum. This suggests the doping with Ca to result in additional peculiarities appearance in band spectrum of $YBa_2Cu_3O_y$.

For explanation the S(T) dependencies obtained we have used additional assumption about slight asymmetry of the conductive band. Taking into account this fact is effected by introduction some distance ($b \cdot W_D$, where b is asymmetry parameter) between centers rectangles D(E) and σ(E). In this case in formula for thermopower (2) instead of μ we must use now (μ-b$\cdot W_D$). The good agreement between the calculated and experimental dependencies of S(T) is demonstrated in Fig.5.

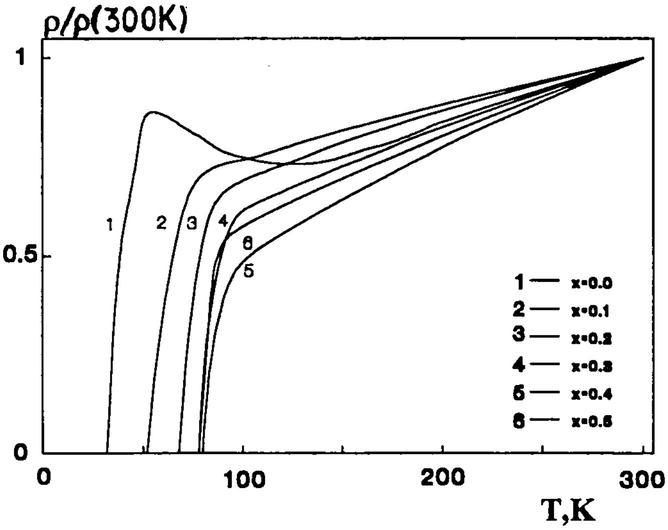

Fig.4. The resistivity vs. temperature in $Y_{1-x}Ca_xBa_{1.5}La_{0.5}Cu_3O_y$

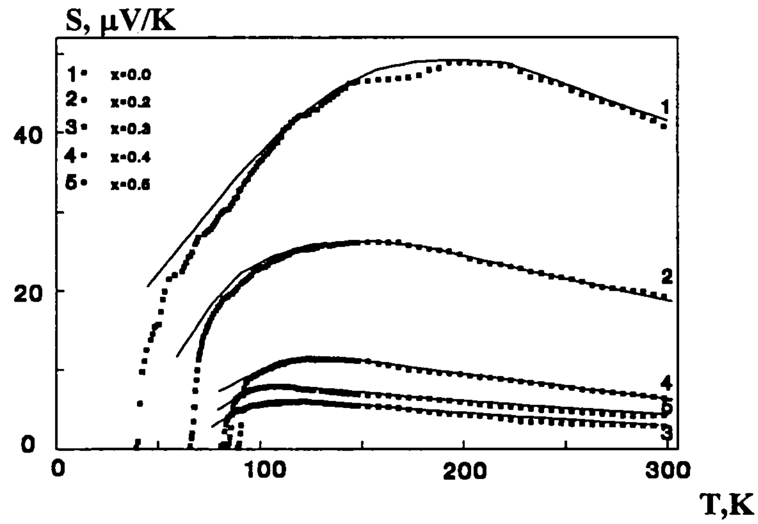

Fig.5. The thermopower vs. temperature in $Y_{1-x}Ca_xBa_{1.5}La_{0.5}Cu_3O_y$

The concentration dependencies of band structure parameters calculated are shown in Fig.6. It can be seen that the Ca content increase causes the total effective band width decreasing and reducing of F value with the slope of the W_D(x) and F(x) dependencies decreasing with x value. Thus, the trends in band spectrum parameters changing (and simultaneously in T_c value changing) are opposite to the ones observed in the systems with single substitutions described above. Nevertheless, two facts have engaged our attention. In the first place, the relation between critical temperature and band spectrum parameters is the same as in single substituted systems. It is to be noted that the practical constancy of T_c is accompanied by sligth changing of band parameters (compare Table 2 and Fig.6 for x=0.3-0.5). And in the second place, the change of all these parameters correlates with oxygen content changing. These things considered, we can explain the results obtained in the frame of our model. Additional Ca doping leads to decrease of oxygen content as compared to single substitution and the over-stoichiometric oxygen escapes from the cell (the y value closes to 7) (see Table 2). As a result the oxygen sublattice becomes more ordered which results in narrowing of the band. Simultaneously band filling degree decreases nearing to half.

Thus, the results obtained confirm the conclusion made earlier (when studying the 3d-metals substitutions for Cu [12]) about the determinant effect of oxygen sublattice condition on band spectrum parameters and superconductive properties of $YBa_2Cu_3O_y$.

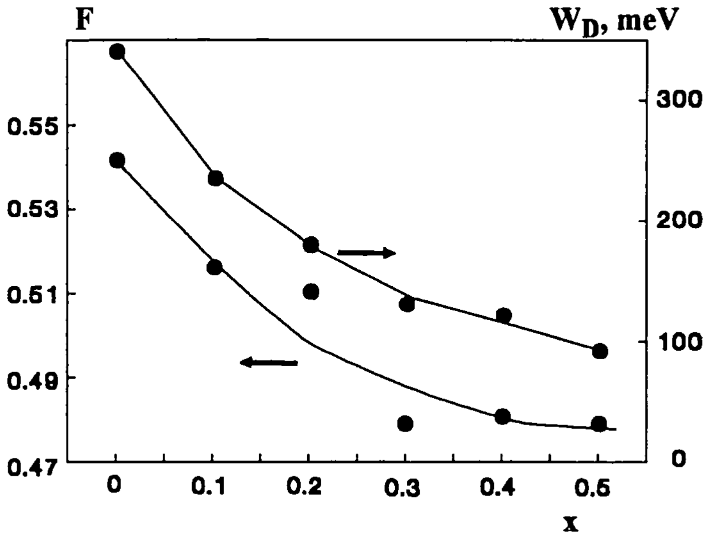

Fig.6. The band parameters vs. Ca content in $Y_{1-x}Ca_xBa_{1.5}La_{0.5}Cu_3O_y$.

For more elucidation of Ca influence on band spectrum transformation we have studied the Ca-doped samples with oxygen deficit (see Table 3). The S(T) dependencies for these samples are shown in Fig.7. The oxygen annealing gave us the possibility to obtain data which may be interpreted in the frame of our model (as indicated by Fig.7 the S values increase after annealing, i.e., the band filling increases and we can use the approximation described above). The features of S(T) dependencies revealed in the double-substitution samples hold in these ones. Besides of this the T_c value increases (see Table 3) and the F value decreases (see Fig.8) with Ca content also. As for the total effective band width our calculation show that its value remains practical constant (W_D=160-190mev). It is necessary to note that oxygen deficit in annealed Ca-doped samples increases rather significantly. According to our conception this fact must cause broadening of the band. However, if the assumption about introduction of additional Ca-states to the band is true, the combination of two effects (broadening of band and increasing of peak of Ca-states which is located in the band) can results in insignificant change of the W_D value which is the effective band width, i.e., the width of rectangle approximating the D(E) function. It can be noted that the calculated value of b parameter depends lineary with Ca content as in the samples with double substitution and the b values for both of these series fall on one trend. This confirms the assumption that it is the calcium that causes the rise of asymmetry of the band introducing additional states.

Table 3.
The oxygen content, parameters of superconductive transition and thermopower in $Y_{1-x}Ca_xBa_2Cu_3O_y$ after annealing.

x	y	T_c^m, K	T_c^o, K	S(300K), μV/K
0.000	6.73	63.7	61.1	17.8
0.025	6.72	70.8	67.9	14.0
0.050	6.70	72.0	69.7	12.4
0.075	6.68	75.1	73.1	13.3
0.100	6.66	80.0	77.3	9.4
0.150	6.58	80.5	74.2	9.3
0.200	6.53	80.9	76.6	8.0

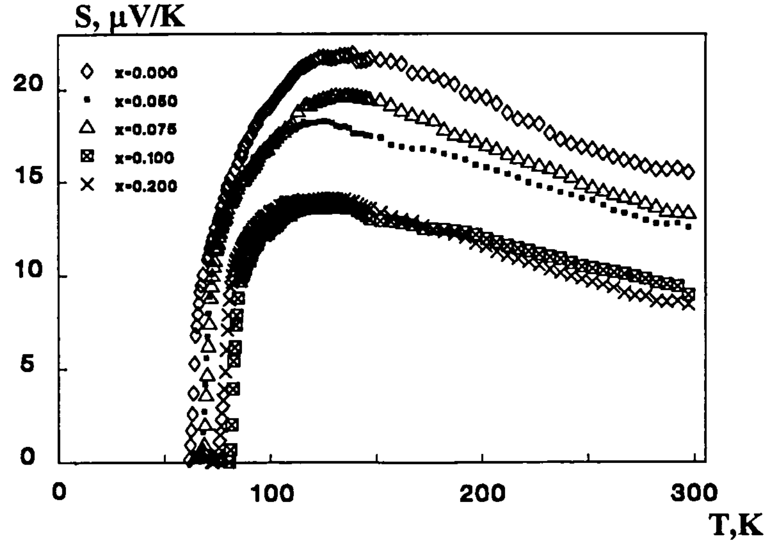

Fig.7. The thermopower vs. temperature in $Y_{1-x}Ca_xBa_2Cu_3O_y$ after annealing.

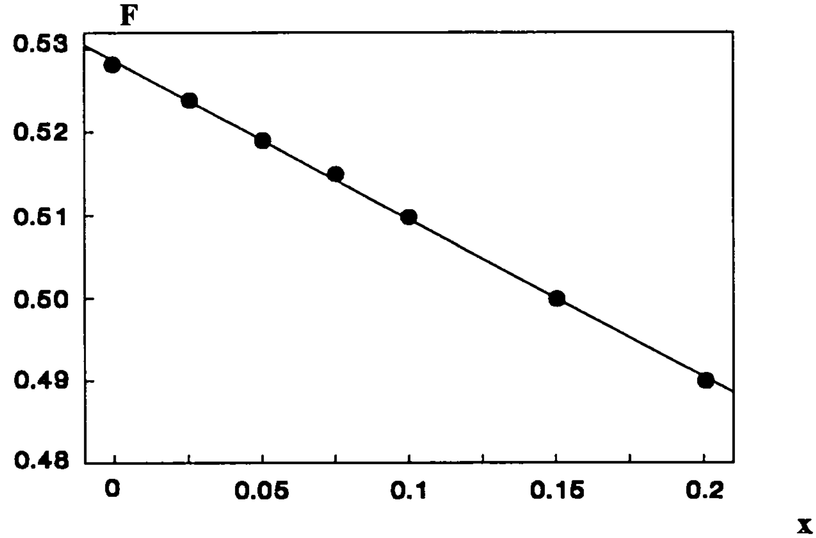

Fig.8. The degree of band filling with electrons vs. Ca content in $Y_{1-x}Ca_xBa_2Cu_3O_y$ after annealing.

The increase of T_c value with x observed in experiment can be explained by two different effects. On the one hand, the band filling nears to half with Ca content increase, i.e., the Fermi level shifts to the DOS function maximum located in the middle of the band and this causes the T_c value increase. On the other hand, the F value decreasing can be explained by arising of the additional Ca-states in the upper half of the band. In this case pinning of the Fermi level in the region of Ca-states is possible. As a result the DOS function value at Fermi level (and correspondingly the T_c value) decreases. For the final answer the question about mechanism of T_c increase observed in the Ca-doped samples the investigations of the samples with more oxygen deficit (for additional shift of Fermi level position in the start sample) is necessary.

4.CONCLUSIONS

In summary, we have performed the investigation of the transport phenomena in Ca-doped samples of the $YBa_2Cu_3O_y$ system with different oxygen content and substitution for Ba by La. The results obtained and their analysis on the basis of narrow band model allow to make the following conclusions.

1. The Ca doping leads to T_c depression in the case of near stoichiometric content and to increasing of T_c if Ca is introduced in the samples with significant deviation from stoichiometry due to oxygen deficit or substitution for Ba.

2. The temperature dependencies of thermopower in Ca-doped samples take some additional features when compared with typical ones for Y-Ba-Cu-O system.

3. The S(T) dependencies analysis on the basis of narrow band model shows that Ca doping causes the increasing of asymmetry degree of the conductive band. The most likely reason of this is additional Ca-states which are located in the region of the band.

4. The character of the critical temperature change in $YBa_2Cu_3O_y$ with dopant content increase correlates with band spectrum parameters change. The possibility of simultaneous explanation of all the experimental results obtained confirms the validity of using the narrow band model for interpretation of transport phenomena data in Y-based HTSC.

5. The conclusion about determinant effect of the extent of oxygen subsystem condition on the band spectrum parameters and critical temperature of $YBa_2Cu_3O_y$ have been confirmed.

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