THE EFFECT OF SUBSTITUTION FOR Cu ON TRANSPORT PROPERTIES AND BAND SPECTRUM $YBa_2Cu_3O_y$

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The temperature dependencies of resistivity $\rho(T)$ and thermopower $S(T)$ of $YBa_2Cu_{3-x}M_xO_y$ (M = Fe, Co, Ni, Mn) have been measured. It was found that all the specific features on the $S(T)$ characteristic of $YBa_2Cu_3O_y$ — the constant or weakly changing S in the region of high temperatures and the presence of the maximum of $S(T)$-remain. In case of M = Fe, Co *the value of $S(T = 300\ K)$ is increasing considerably with x, while in case of* M = Ni, Mn *the $S(T = 300\ K)$ change with x is negligible. The results obtained have been interpreted within narrow band model, developed earlier by the authors for $YBa_2Cu_3O_y$ with various oxygen content. This permitted to determine the values of the electron spectrum parameters; conductive band width W, band filling with electrons, F, and state delocalization degree, C — and to observe their change with x for different dopants. Analyzing the results obtained we found that in the case of doping with* Fe *or* Co *(when T_c decreases with x drastically) W and F increase considerably with x, and C decreases. In the case of doping with* Ni *or* Mn *(when T_c decreases with x noticeably slower) the electron spectrum parameters change very negligibly. It follows that the dopants causing the oxygen sublattice disordering (*Fe *and* Co*) influence superconductive properties and band spectrum more considerably that the dopants which do not cause this disordering (*Ni *and* Mn*).*

Introduction. The specific features of the transport coefficients behavior of Y–Ba–Cu–O system suggest an idea that the transport and superconductive properties are governed by a narrow peak in the density of states. The model of the narrow allowed energy band, which had been used before to account for the behavior of the transport coefficients of $YBa_2Cu_3O_y$ [1], permits to determine the values of electron spectrum parameters (the conductive band width, W_D, the band filling with electrons, F, and state delocalization degree, C) from the analysis of the temperature dependences of the thermoelectric power. The analysis of the transport coefficients behavior in $YBa_2Cu_3O_y$ with various oxygen content and conclusions about the principal features of the structure of Y–Ba–Cu–O system (and about the mechanism of the oxygen deficit influence on the electron spectrum parameters) were made by the authors in [2]. In this paper we carried out the comparative analysis of the changes in the band spectrum parameters with substitution for copper by different $3d$-metals (Fe, Co, Ni, Mn). The results obtained were compared with the literature data about the crystal structure of $YBa_2Cu_3O_y$ transformation with this substitution.

Results and discussion. X-ray diffraction spectra indicate that the samples of $YBa_2Cu_{3-x}M_xO_y$ (M = Fe, Co, Ni) are single-phased for $x \leq 0.3$. Extra phases in $YBa_2Cu_{3-x}Mn_xO_y$ are revealed above $x = 0.2$. Further we will discuss only the results obtained for single-phased samples.

The oxygen content in $YBa_2Cu_{3-x}Fe_xO_y$ was determined by the thermogravimetric analysis and by the neutron diffraction studies (in $YBa_2Cu_{3-x}Mn_xO_y$ — only by TGA). The oxygen content increases with x in the Fe-doped samples (from $y = 6.94$ at $x = 0.0$ to $y = 7.05$ at $x = 0.30$) and changes slightly near $y = 6.94$ in Mn-doped samples. Since these data are in quantitative agreement with the results reported by other authors and the conditions of preparing of all the series are the

same, we suppose the character oxygen content changing in Co- and Ni-doped samples to be analogous with that described in the literature.

The temperature dependences of resistivity $\rho(T)$ are linear or almost linear in a wide range of temperatures. The increase of Fe or Co content is accompanied by an increase in the values and changes in the temperature dependences of ρ and by fairly rapid suppression of the critical temperature T_c (see Fig. 1 for $YBa_2Cu_{3-x}Co_xO_y$). The dependences $\rho(T)$ for Ni- and Mn-doped samples (in which T_c changes fairly slightly with the dopant content increase) remain linear for all the dopant concentrations studied (see Fig. 2 for $YBa_2Cu_{3-x}Mn_xO_y$).

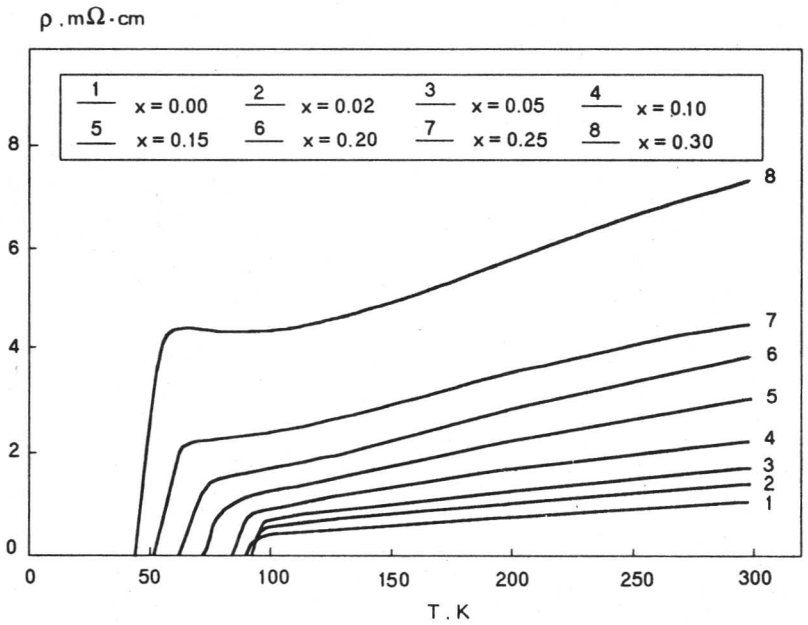

Fig. 1. Resistivity vs temperature for $YBa_2Cu_{3-x}Mn_xO_y$

The dependences of T_c (determined by the midpoint of the $\rho(T)$-transition) on different dopant content x are given in Fig. 3. It is to be noted that up to $x(F) \leq 0.03$ and $x(Co) \leq 0.07$ T_c remains almost constant and then drops rapidly. For the Ni- and Mn-doped samples T_c decreases much more slowly and dependences $T_c(x)$ are almost linear.

The important features distinguishing $YBa_2Cu_3O_y$ from ordinary metals are weak dependence $S(T)$ or virtually constant value of S in a wide range of temperatures and the maximum of $S(T)$ observed at low temperatures (higher that T_c). These features persist at doping (it is shown in Fig. 4 and in Fig. 5).

With the Fe (or Co) content increase the absolute magnitude of S increases significantly and maximum of $S(T)$ shifts to higher temperatures (see Fig. 4 for $YBa_2Cu_{3-x}Fe_xO_y$). This transformation of dependences is analogous to that observed in $YBa_2Cu_3O_y$ with the oxygen deficit increase.

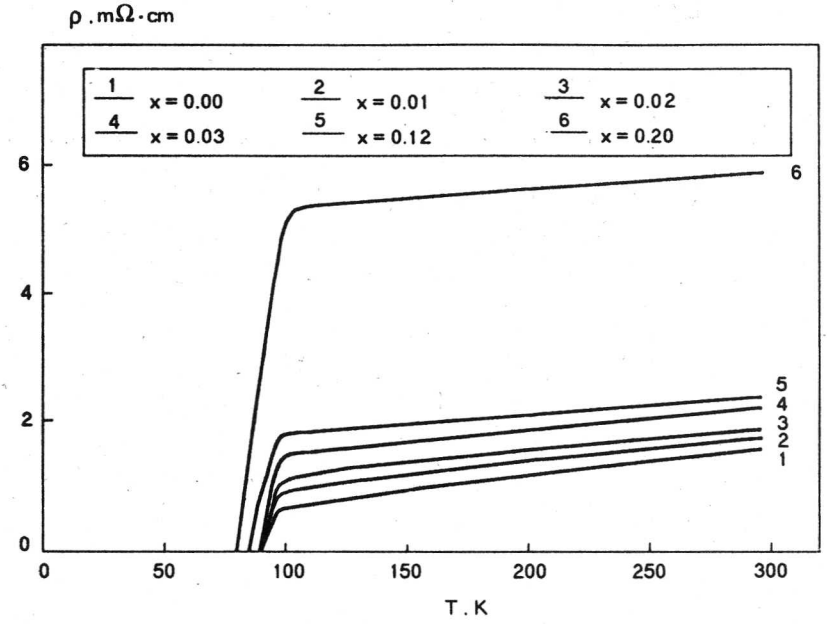

Fig. 2. Resistivity vs temperature for $YBa_2Cu_{3-x}Mn_xO_y$

With Ni (or Mn) content increase the absolute magnitude of S changes very slightly (see Fig. 5 for $YBa_2Cu_{3-x}Ni_xO_y$). Fig. 6 shows the different effects of different dopants on the magnitude of S_{300} .

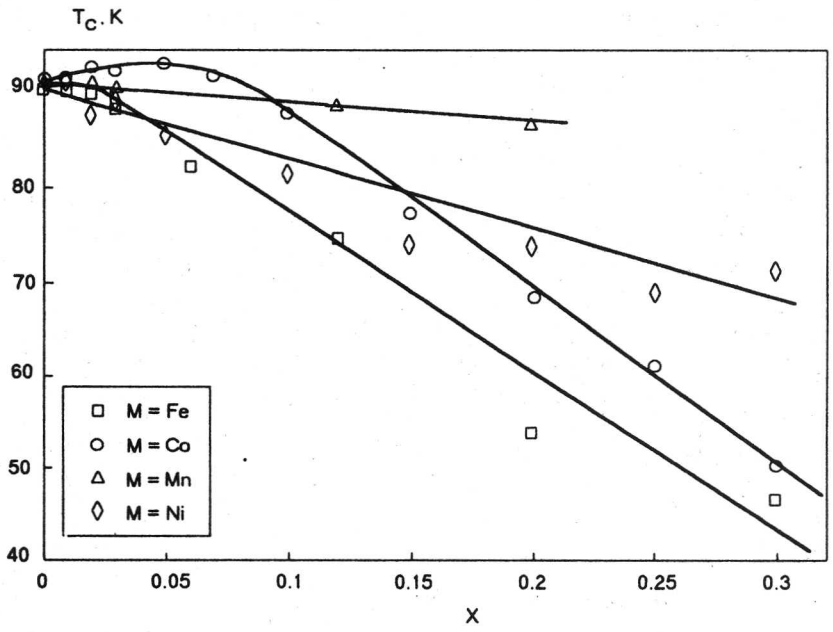

Fig. 3. Variation of T_c with dopant content in $YBa_2Cu_{3-x}M_xO_y$

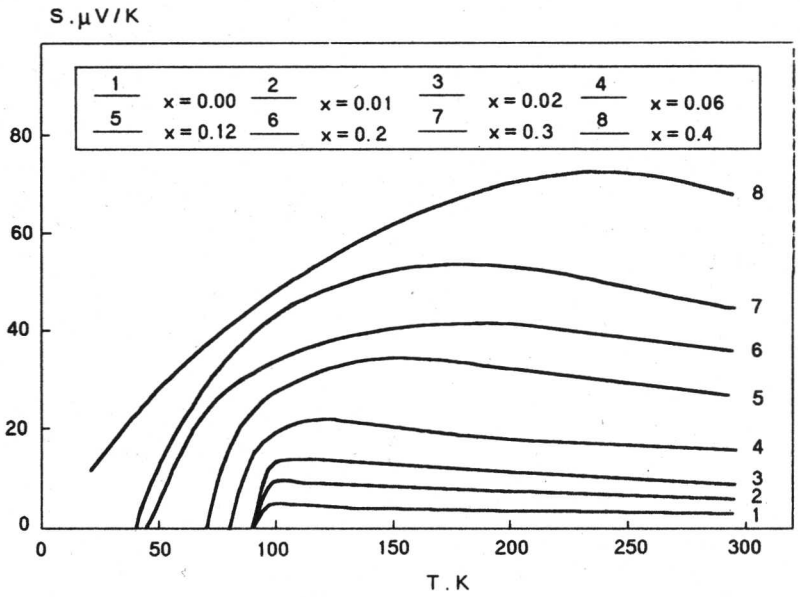

Fig. 4. Thermopower vs temperature for $YBa_2Cu_{3-x}Fe_xO_y$

Owing to similarity with the results obtained for the undoped system the results described may be interpreted within the narrow band model mentioned above.

This model assumes the transfer of change carriers along the band whose width is much less than in usual metals or semiconductors (comparable to the k_BT value).

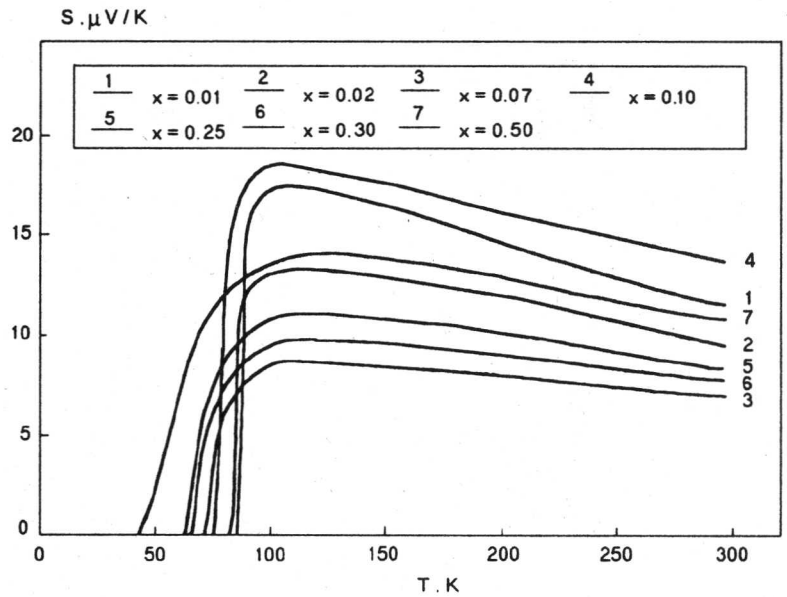

Fig. 5. Thermopower vs temperature for $YBa_2Cu_{3-x}Ni_xO_y$

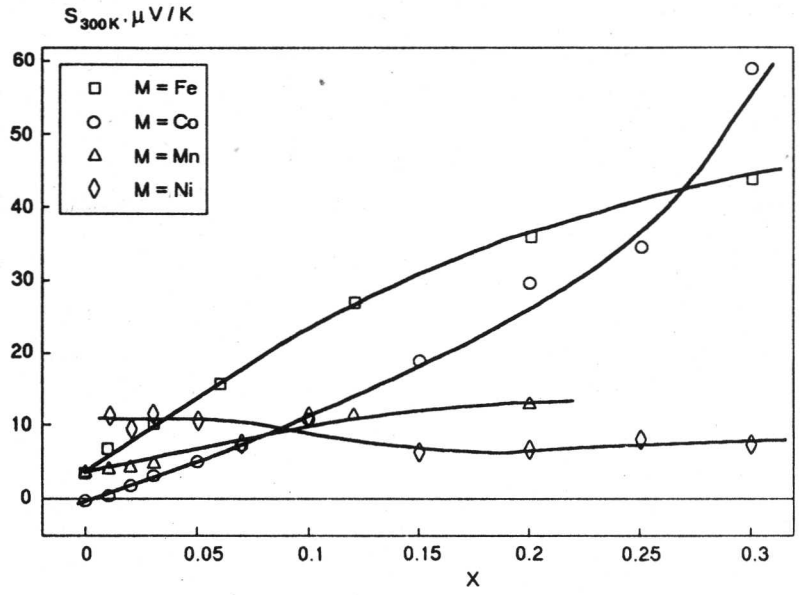

Fig. 6. Variation of the thermopower at T = 300 K with dopant content in $YBa_2Cu_{3-x}M_xO_y$

The charge carrier concentration is believed to remain constant with the temperature change and is determined by the band filling with electrons F . This parameter is equal to the ratio of the numbers of electrons to the numbers of states in the band, and for the superconductive $YBa_2Cu_3O_y$ accepting the value within the internal $F = 0.5 \div 0.65$, which corresponds to the hole conductivity. The value of F determines the value and the sign of the thermopower in the region of high temperatures when $S(T) \approx$ const according with the formula:

$$S \approx -k_B/e \cdot \ln [(1 - F)/F] .$$

Thus, changes of F (and respectively, S_{300}) occurring with the deviations from the $YBa_2Cu_3O_y$ stoichiometric content (oxygen deficit increase, doping with various elements) results from the changes of the conduction band parameters and the number of carriers in the band. Also, the narrow band model allows one to determine from the comparison between the experimental and the calculated $S(T)$ dependences the effective values of the complete band width W_D , and the width of the delocalized (conductive) states band W_σ which is usually smaller than the complete band width ($C \equiv W_\sigma / W_D < 1$); this may be due to a different nature of energy dependences of the density of states (DOS) and the differential conductivity functions, as well as the probable localization of the states near the band edge caused by a disordering in the lattice. In $YBa_2Cu_3O_y$ with $y \approx 7$ Fermi level E_F is situated in the middle of the band near the maximum of the DOS function $D(E)$. In this case $F \approx 0.5$ and the band energy parameters are $W_D \approx 70 \div 90$ meV and $W_\sigma \approx 30 \div 40$ meV [3]. With decrease in oxygen content y the number of charge carriers (holes) decreases (the value of F increases which leads to the E_F

displacement from the middle of the band (the $D(E)$ 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 [4], this leads to the localized states share increase (in our model this corresponds to the C parameter value decrease). The complete band width increases in this case which causes the general drop of the DOS including $D(E_F)$. It is the band broadening caused by disordering that is the basic factor leading to the $D(E_F)$ value decrease, as the complete possible range of F values in the superconductive $YBa_2Cu_3O_y$ is sufficiently low. The $D(E_F)$ value decrease, in its turn, leads to the T_c value drop.

Dopant concentration dependencies of the conductive band width and of the band filling with electrons obtained by the calculations based on the narrow band model are given in Fig. 7 and Fig. 8. Analyzing these dependences one can conclude that the dopants studied can be separated into two groups according to the extent of their influence on the band structure parameters.

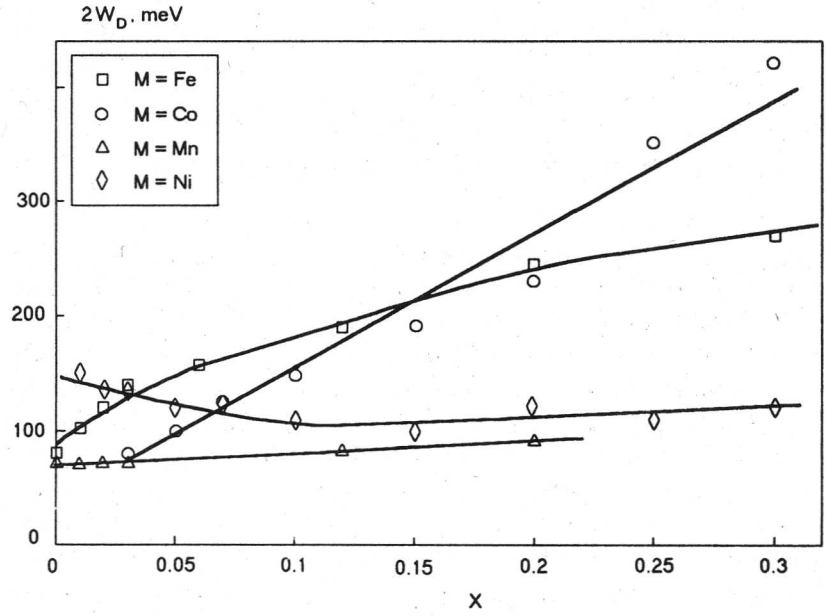

Fig. 7. Band width vs dopant content in $YBa_2Cu_{3-x}M_xO_y$

Substitution of Cu by Fe or Co results in significant broadening of the band and considerable increase of F , which is analogous with the influence of oxygen deficit. The value of W_D increases mainly by increasing of share of localized states. Substitution of Cu by Ni or Mn does not lead to significant changing of the band width. With the Ni content increase the value of F also changes very slightly. The reasons of considerable increasing of F with the Mn content increase will be discussed below.

These two groups of dopants are known to be different in their influence on the oxygen sublattice. The samples of $YBa_2Cu_{3-x}M_xO_y$ (M = Fe, Co) undergo an orthorombic-tetragonal transition at $x \simeq 0.12$ (M = Fe) and $x \simeq 0.09$ (M = Co). For low values of x Fe replaces Cu preferentially in the Cu(1) sites whereas for

higher concentrations, $x > 0.05$, $10 \div 20\%$ of Fe ions occupy Cu(2) sites. It is well established that Co substitutes for Cu preferentially in the Cu(1) sites. Since Fe(Co) ions in Cu(1) sites show a preference for higher coordination than four, such a substitution results in disordering of the oxygen sublattice: the previously unoccupied O(5) are filled both by oxygen atoms from atmosphere during annealing and by oxygen atoms from neighboring units without Fe(Co). Thus the oxygen concentration increases with these dopants content increase.

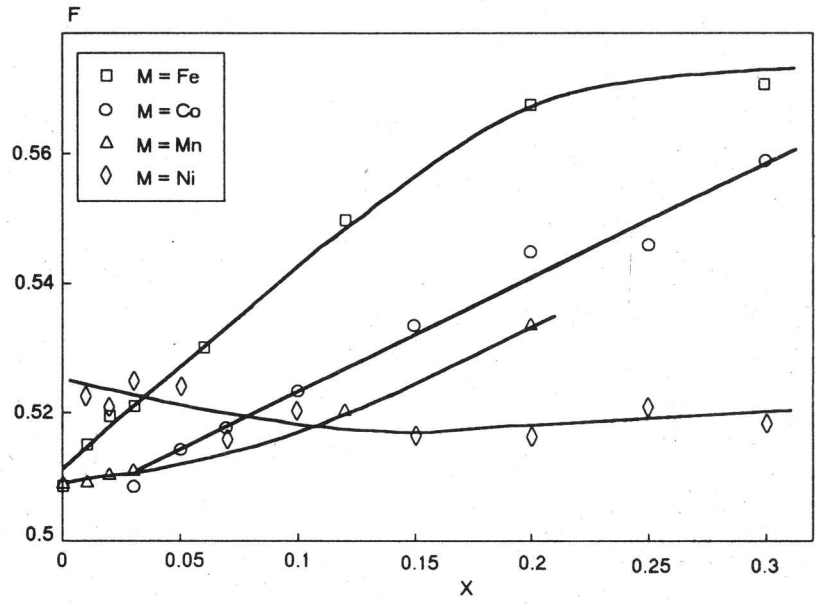

Fig. 8. Band filling with electrons vs dopant content in $YBa_2Cu_{3-x}M_xO_y$

Samples of $YBa_2Cu_{3-x}M_xO_y$ (M = Ni, Mn) remain orthorombic throughout the range of possible compositions. The preferred site for Ni and Mn in the 123 compound is the Cu(2) site. The oxygen content in Ni- and Mn-doped samples remains constant throughout the range of solid solution.

Thus the gradual disordering of oxygen sublattice resulting from oxygen content increase and redistribution of its atoms in lattice in case of substituting for Cu by Fe or Co is not observed in case of substituting for Cu by Ni or Mn.

Comparing these data with the dopant concentration dependences of the band structure parameters obtained in this paper one can conclude that it is the dopant disordering the oxygen sublattice that influence the band structure parameters greatly. It follows that the oxygen sublattice condition has a determinant effect on the band spectrum structure of $YBa_2Cu_3O_y$.

Further we will discuss fine features of dopant concentration dependences of band structure parameters.

Fig. 8 shows that the dependences $F(x(\mathrm{Co}))$ and $F(x(\mathrm{Fe}))$ are similar, but somewhat displaced with respect to one another. It seems to be caused by following. The values of S of these two series initial samples are different; ($S_{300} = 3.4\,\mu\mathrm{V/K}$ for M = Fe and $S_{300} = -0.5\,\mu\mathrm{V/K}$ for M = Co); it follows that the oxygen contents in these samples are also different ($y = 6.93$ and $y = 7.00$

respectively). Hence the preparation conditions of these series were not the same. Comparing the dependences $W_D(x(\mathrm{Fe}))$ and $W_D(x(\mathrm{Co}))$ one can see that in the region of high dopant concentrations the band width for $YBa_2Cu_{3-x}Fe_xO_y$ increases with x slower than for $YBa_2Cu_{3-x}Co_xO_y$ (see Fig. 7). It can be explained as follows: atoms of Co replace Cu preferentially in the Cu(1) sites throughout the range of possible compositions, whereas above a certain concentration of Fe ($x = 0.12$) its atoms begin to replace Cu in both sites. Hence beginning from this value of x(Fe) an extent of dopant influence on oxygen sublattice decreases — for which reason the band width increases slower.

The difference in the values of W_D for Ni- and Mn-doped samples is explained also by different oxygen content. The considerable increase of F with Mn content increase can be caused by that the valence of Mn-ions is likely to be higher than the valence of Cu-ions. It is to be noted that according to some data the formal valence of Mn in this system is four.

Comparing the dopant concentration dependences of band structure parameters (Fig. 7, 8) and of critical temperature T_c (Fig. 3) one can reveal the interrelation between them. The considerable increase of the band width (and the band filling with electrons) with Fe (or Co) content increase is accompanied with the rapid drop of T_c. The weak changing of band structure parameters with Ni content increase is accompanied with fairly slow decrease of T_c. For $YBa_2Cu_{3-x}Mn_xO_y$ even the considerable increase of F accompanied by the weak changing of band width do not lead to rapid drop of T_c. The results obtained are seen to be in good agreement with our model, which connects the conductive band transformation in $YBa_2Cu_3O_y$ with realization of the Anderson's localization of states mechanism. In this case the increase of F (the E_F displacement from the middle of the band — the $D(E)$ function maximum — to its upper edge) and the increase of lattice disordering leading to the band broadening have to lead to a decrease in value of $D(E_F)$ and consequently in value of T_c. It is to be noted that it is the broadening of band that plays a main role in decrease of T_c. It is proved by the results obtained for $YBa_2Cu_{3-x}Mn_xO_y$ for which the increase of F accompanied by the weak increase of W_D do not lead to rapid drop of T_c.

Conclusions.

1. In this work we carried out the comparative investigation of the influence of substitution for Cu by different 3*d*-metals (Fe, Co, Ni, Mn) on transport properties of $YBa_2Cu_3O_y$.

2. The temperature dependences of resistivity ρ and thermopower S in $YBa_2Cu_{3-x}M_xO_y$ (and the character of their changing with dopant content) were found to be similar to those for $YBa_2Cu_3O_y$ with different oxygen content. It justifies the application of the narrow band model for describing the transport properties of Y–Ba–Cu–O system in a normal phase.

3. Analyzing the extent of dopant influence on conductive band structure and superconductive properties we can separate the dopants studied into two groups. The Fe(Co) content increase (Fe and Co replace Cu preferentially in the Cu(1) sites and induce the considerable disordering of oxygen sublattice) leads to significant broadening of the band and to an increase of the band filling with electrons. It is accompanied by the rapid drop of T_c. Ni and Mn replacing Cu in

the Cu(2) sites and not inducing considerable changing of $YBa_2Cu_3O_y$ structure influence the band structure parameters much more weakly and to slower decreasing of T_c with its content increase.

4. To a considerable extent the rapid decreasing of T_c in $YBa_2Cu_{3-x}(Fe, Co)_xO_y$ is determined by the disordering in lattice caused by this a substitution. The localization of states caused by the disordering together with other factors (first of all, the changing of F) have a considerable effect on the value of T_c in Y–Ba–Cu–O system.

5. Analyzing the character of the band structure parameters changing with different dopant content increase and taking into account the crystallochemical studies data we can conclude that the oxygen sublattice condition has a determinant effect on band structure parameters and superconductive properties of $YBa_2Cu_3O_y$.

1. *Kazmin S. A., Kaidanov V. I., and Leising G.*, Sov. Phys. Solid State 30, 1703 (1988) [Fiz.Tverd.Tela 30, 1295 (1988)].
2. *Gasumyants V. E., Kazmin S. A., Kaidanov V. I. et al.*, Sov. Superconductivity 4, 1184 (1990) [Sverkhprovodimost' 4, 1280 (1990)].