THE BAND SPECTRUM OF Bi-BASED SUPERCONDUCTORS

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The temperature dependencies of resistivity $\rho(T)$, thermopower $S(T)$ and Hall coefficient $R(T)$ of Bi-based high-T_c superconductors (HTSC) have been measured. We have investigated the single-phase samples of both 2212 and 2223 types. It was found that $\rho(T)$ and $R(T)$ dependencies of the sample of Bi-system are similar to Y–123. Deviations from the stoichiometric contents (oxygen deficit increase in Y–123, substitution for Ca in Bi-2212) lead to the same transformations of $\rho(T)$ and $R(T)$ dependencies. On the other hand, the temperature dependencies of thermopower in the region of small $|S|$ values (characteristic of both 2212 and 2223 phases near stoichiometric content) are essentially different. However, substitution of Ca by Nd and Y in the Bi–2212 phase causes increase of S values. In this case $S(T)$ dependence becomes similar to that of Y–123. This fact suggests that narrow band model (the band width comparable to the k_BT value) developed by the authors for explaining peculiarities of Y–123 transport phenomena may be used to Bi–based HTSC. The nature of $S(T)$ dependencies for small $|S|$ values appears to be explained by asymmetry of the band, which is especially noticeable, when it is half–filled (when the Fermi level is near the middle of the band). The obtained results indicate that the band width, the correlation between its increasing and the value of T_c decreasing and also the nature of occurring variation with the deviations from stoichiometric–content electron–system parameters were found to be similar in Y– and Bi–based HTSC.

It is hard to tell now something definite about the band structure in the vicinity of Fermi level of the Bi–based high-T_c superconductors. The complex experimental investigation of the transport phenomena is one of the mostly used for the band spectrum study and is reasonably effective. This is confirmed by experience of the investigations of semiconductors and semimetals with complicated electron spectra. The information, extracted from such investigations, becomes more detailed and unambiguous if we can vary the Fermi level position over a wide range of energies. This is usually achieved by doping materials under study with donor or acceptor impurities.

To realize this approach, as applied to the Bi–system, we have chosen 2212–phase ($T_c \simeq 60 \div 80$ K) as a main object of the investigation. Compared to 2223–phase ($T_c \simeq 105 \div 110$ K) this one is more stable, which enables us to prepare highly doped samples being single–phase. The samples compositions corresponded to the formula $Bi_2Sr_2Ca_{1-x}M_xCu_2O_y$ (M = Nd,Y) with $0 \le x \le 0.5$. The single–phase samples of 2223–phase have been studied, but these were the undoped ones as well. In both cases the samples studied were ceramics. The absence of heterogeneous phases in the appreciable amount was controlled by using the X–ray–phase analysis and by comparing the temperature dependencies of the magnetic susceptibility with ones of transport coefficients.

Fig. 1 shows the critical temperature $T_c(\rho = 0)$ dependence on the dopant content. T_c is decreased as Y or Nd content increases in accordance with the published data [1–4].

Fig. 2 shows the typical temperature dependencies of the Seebeck coefficient (S) for undoped samples of 2212 and 2223 systems. Sample numbers are the same as in Table 1. Temperature dependencies of resistivity (ρ), Seebeck and Hall (R) coefficients for the $Bi_2Sr_2Ca_{1-x}M_xCu_2O_y$ samples in the case of M = Nd are plotted in Fig. 3. Results obtained for M = Y are qualitatively analogous.

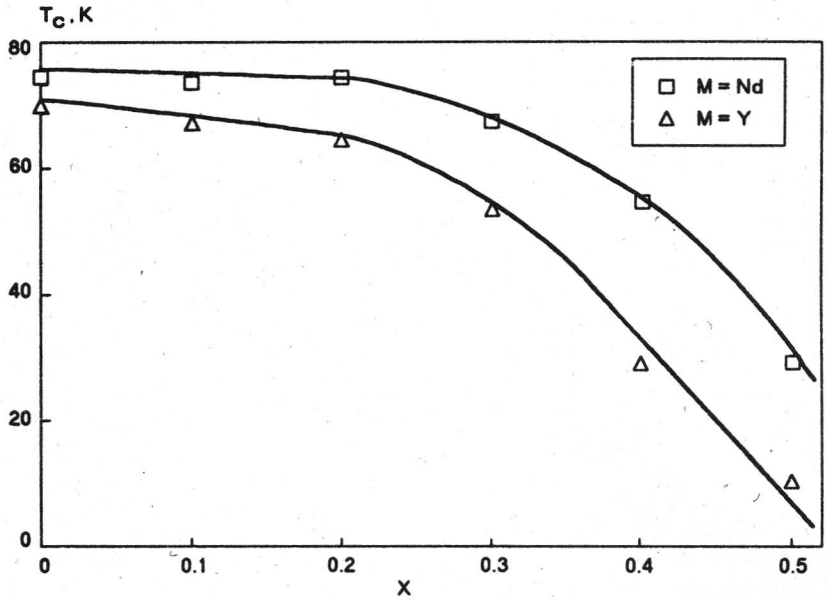
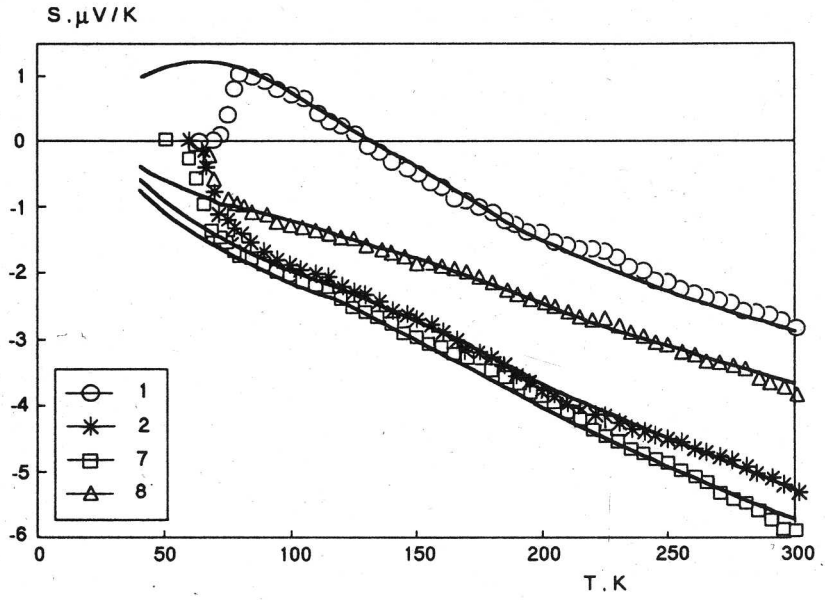


Fig. 1. Variation of T_c with dopant content in $Bi_2Sr_2Ca_{1-x}M_xCu_2O_y$

At first, we consider the results, obtained for undoped samples. It should be noted that there are some peculiarities in the transport coefficients behaviour,

Table 1. The narrow band model parameters for undoped samples ($C = 0.4$ for all the samples).

Phase, number	F	$2W_D$, meV	b	Phase, number	F	$2W_D$, meV	b
2212				2223			
1	0.4800	60	-0.023	1	0.4670	115	-0.046
2	0.4685	80	-0.028	2	0.4656	130	-0.045
3	0.4765	65	-0.024	3	0.4620	120	-0.049
4	0.4686	78	-0.027	4	0.4680	115	-0.050
5	0.4785	65	-0.025	5	0.4668	115	-0.046
6	0.4682	70	-0.027	6	0.4655	125	-0.044
7	0.4682	80	-0.028	7	0.4617	115	-0.049
8	0.4760	80	-0.022	8	0.4682	115	-0.051



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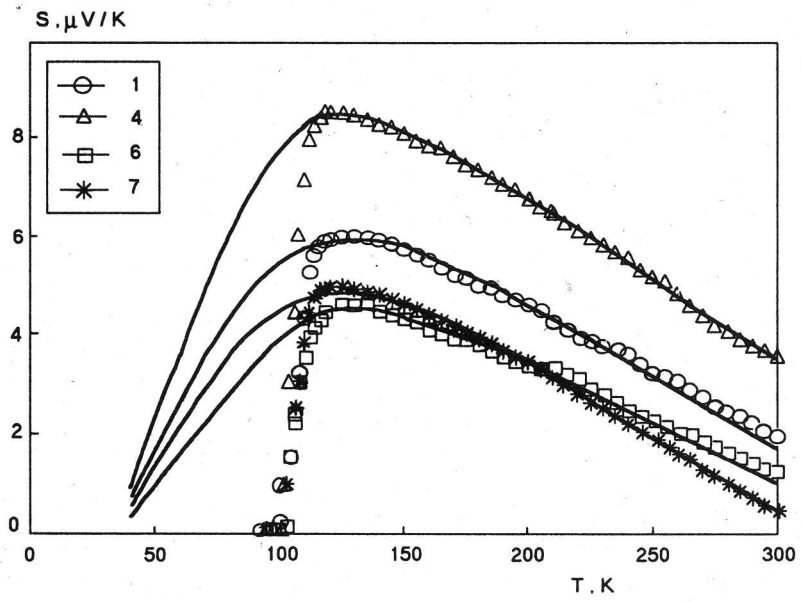


b

Fig. 2. Thermopower vs temperature for Bi-based superconductors: *a* — 2212-phase, *b* — 2223-phase. ○, *, △, □ — experiment, —— — calculation

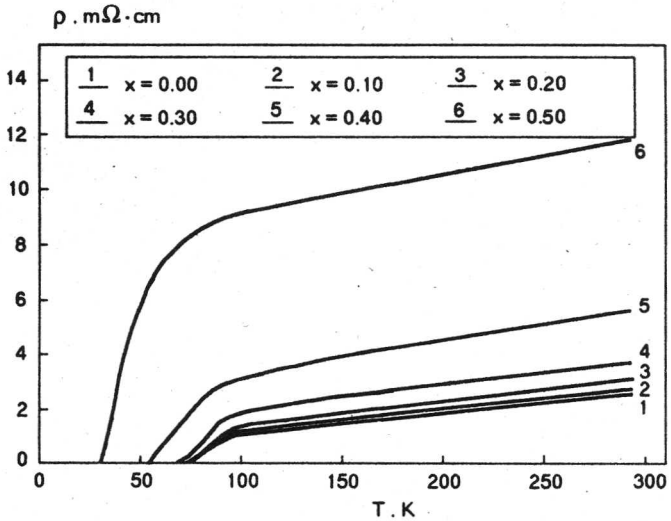
which are similar to those for Y–Ba–Cu–O systems and are quite unusual for ordinary metals, semiconductors and semimetals.

1. Dependence $\rho(T)$ is linear or almost linear in a wide temperature range.

2. Seebeck coefficient values depend on temperature quite slightly. However, one can observe a peak on $S(T)$ curve at the temperature point somewhat higher than T_c . As the dopant content is increased, this maximum is smeared and shifts towards the higher temperature values.

3. The Hall coefficient is decreased with temperature, although the relative lowering of R for Bi–systems is not as great as for Y–Ba–Cu–O samples.

It is desirable to explain these singularities taken together and to describe them quantitatively using the simplest model with the lowest number of fitting



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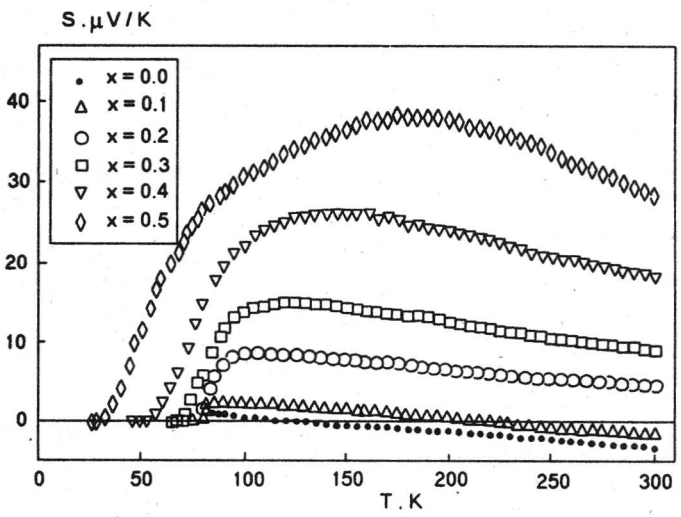

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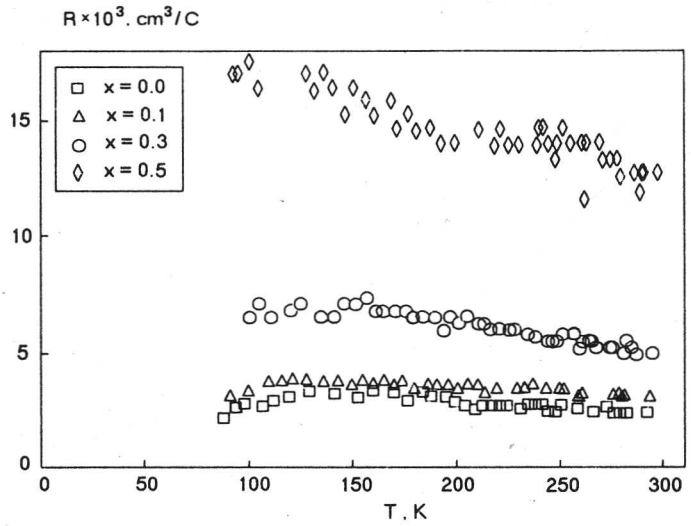


c

Fig. 3. Temperature dependencies of the transport coefficients in $Bi_2Sr_2Ca_{1-x}M_xCu_2O_y$: *a* — resistivity, *b* — thermopower, *c* — Hall coefficient

parameters. For this purpose we can use (as in case of $YBa_2Cu_3O_y$) the narrow-band model, which suggests the band width to be comparable with Fermi smearing.

The analysis of the main electron transport peculiarities in the narrow-band case is performed in Ref. [5]. Some of the concepts and results of this analysis are as follows.

The model includes three phenomenological parameters. The first one is the relation of the free electron density (n) to the whole number of band states (N). This parameter is denoted by $F = n/N$ and is termed as the band occupancy degree, or simply the occupancy degree. Two other parameters symbolized as $2W_D$ and $2W_\sigma$ are the "state density" and "conductivity–effective" band widths. These effective widths may differ one from another as well as from the whole band width $2W$. The distinctions between W, W_D, W_σ are related to the peculiarities and differences in energy dependencies of the electron state density $D(E)$ and the differential conductivity $\sigma(E)$. W_D and W_σ values may be compared to get some information on peculiarities of electron kinetics, dynamics and scattering.

In Ref. [5] some analytical expressions for transport coefficients for the narrow band model were presented. The simplest approximation of $D(E)$ and $\sigma(E)$ functions was used there, namely, it is assumed that these functions are more, than zero (and of constant values) in the energy intervals $-W_D \le E \le W_D$ and $-W_\sigma \le E \le W_\sigma$ respectively and are equal to zero outside these intervals. The numerical computations for the more realistic band spectrum models show that the spectrum details, like $D(E)$ and $\sigma(E)$ peculiarities, are not of great significance as long as W_D and W_σ values are not much greater, than k_BT value.

The equations from Ref. [5] used here are the following:

$$\mu^* = \ln \frac{\mathrm{sh}\,(F/T^*)}{\mathrm{sh}\,\left((1-F)/T^*\right)}, \tag{1}$$

$$\rho = \frac{1}{\langle\sigma\rangle} \cdot \frac{1 + e^{-2\mu^*} + 2e^{-\mu^*} \cdot \mathrm{ch}\,(C/T^*)}{e^{-\mu^*} \cdot \mathrm{sh}\,(C/T^*)}, \tag{2}$$

$$S = -\frac{k_B}{e} \cdot \left\{ \frac{(C/T^*)}{\mathrm{sh}\,(C/T^*)} \cdot \left[e^{-\mu^*} + \mathrm{ch}\,(C/T^*) - \frac{T^*}{C} \cdot \left(\mathrm{ch}\,(\mu^*) + \mathrm{ch}\,(C/T^*) \right) \times \right. \right.$$

$$\left. \left. \times \ln \frac{e^{\mu^*} + e^{C/T^*}}{e^{\mu^*} + e^{-C/T^*}} \right] - \mu^* \right\}, \tag{3}$$

$$R = \frac{\langle\sigma_H\rangle}{\langle\sigma\rangle^2} \cdot \frac{(z-1)(v-1)^2(1+zw)^2(z+w)^2}{z(1+z)(z+v)(1+zv)(w^2-1)^2}, \tag{4}$$

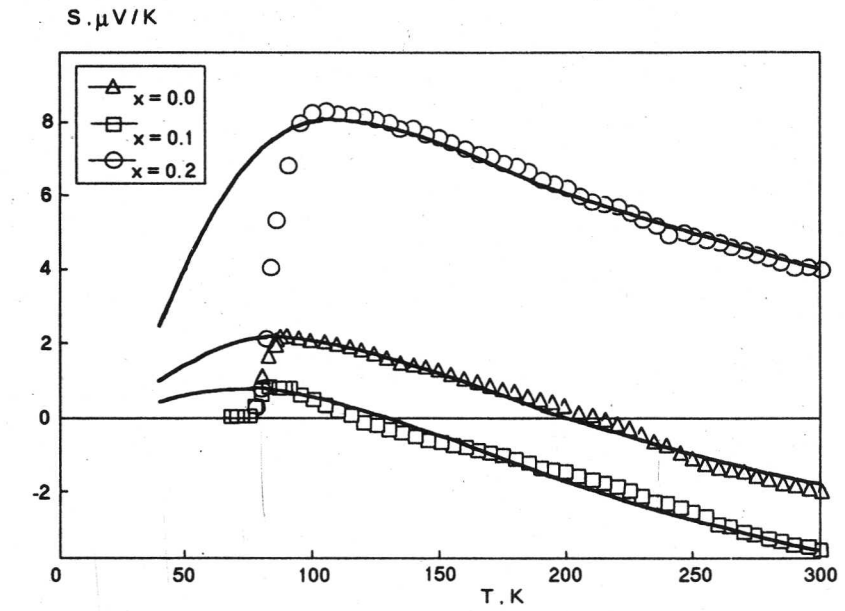
where $\mu^* \equiv \mu/k_BT$ is the reduced chemical potential of electrons; $\langle\sigma\rangle$, $\langle\sigma_H\rangle$ — constant values; $C \equiv W_\sigma / W_D$; $T^* \equiv k_BT/W_D$; $z \equiv \exp(\mu^*)$; $v \equiv \exp(W_{\sigma_H}/k_BT)$; $w \equiv \exp(W_\sigma/k_BT)$.

These equations are valid, if we suppose the band to be symmetric, that is, the centers of gravity of $D(E)$ and $\sigma(E)$ rectangular positions on the energy scale coincide. The asymmetric band was modeled in Ref. [5] by introducing some distance between the centers of the rectangles. If the $D(E)$ rectangle center position is taken to be $E = 0$, then Eq. (1) gives the position of μ at this energy scale, as previously. The expressions used to compute ρ, S and R (Eqs. (2)–(4)) retain their previous form, but everywhere instead of μ^* we must use now $\mu^* - 2bW_D$, where $2bW_D$ is the energy distance between $\sigma(E)$ and $D(E)$ rectangle centers.

The parameters F, W_D, W_σ and b variation in Eqs. (1)–(4) enabled us to calculate the S, ρ , R temperature dependencies being in good agreement with the experimental data as one can see from Figs. 2, 4 for the Seebeck coefficient. In this way we also have estimated parameter values for each sample and so have established the dependencies of parameters on the sample composition.

Some additional remarks are to be made. In the first place it is to be noted that Eq. (3) enabled us to compute the absolute value and the sign of the Seebeck coefficient at different temperatures, whereas ρ and R could be computed only to the accuracy of a constant cofactor. Therefore, we used $S(T)$ dependence to determine F, W_D, W_σ , b values and, then, we verified their validity by comparison of calculated and experimental temperature dependencies of the reduced coefficients: $\rho(T)/\rho(300\ \mathrm{K})$, $R(T)/R(300\ \mathrm{K})$. Almost in all cases the agreement was reasonably good.

Secondly, consideration of the band asymmetry is necessary to explain behavior of transport coefficients for the samples with low values of $|S|$, corresponding to near the half occupancy degree. In this case a slight asymmetry ($b \ll 1$) is sufficient to change the Seebeck coefficient sign at the same band–occupancy degree F. At the same time this slight asymmetry does not practically influence the behaviour of S and other transport coefficients, when the S value is of order of $10\,\mu\mathrm{V/K}$ or higher, i.e., the Fermi level is not very close to the band middle. This is the case of highly doped samples.



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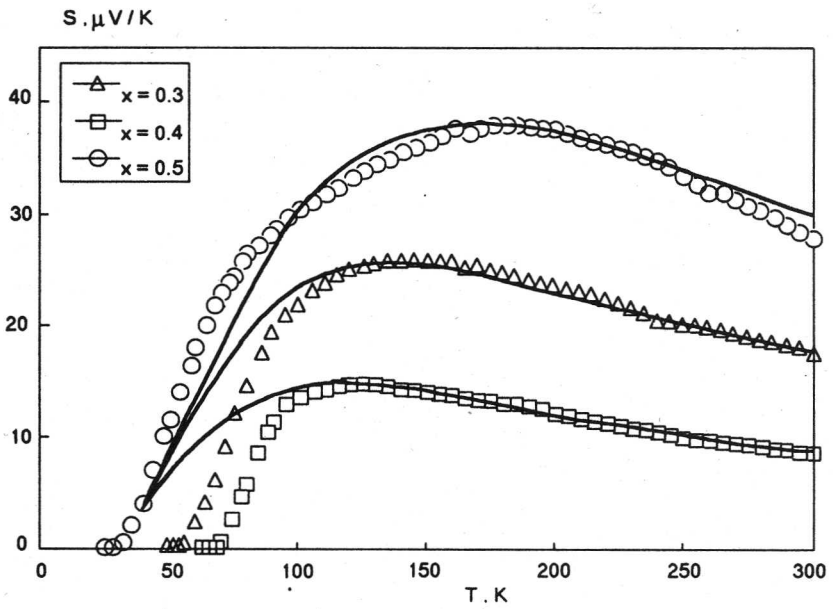


b

Fig. 4. Thermopower vs temperature for $Bi_2Sr_2Ca_{1-x}M_xCu_2O_y$. □ , △ , ○ — experiment, —— — calculation

At last it should be mentioned that the fitting parameters are believed to be temperature–independent. This means that the parameters number is less, than the number of equations which we can use for their determination, because we compare the calculated and experimental temperature dependencies in a wide temperature range.

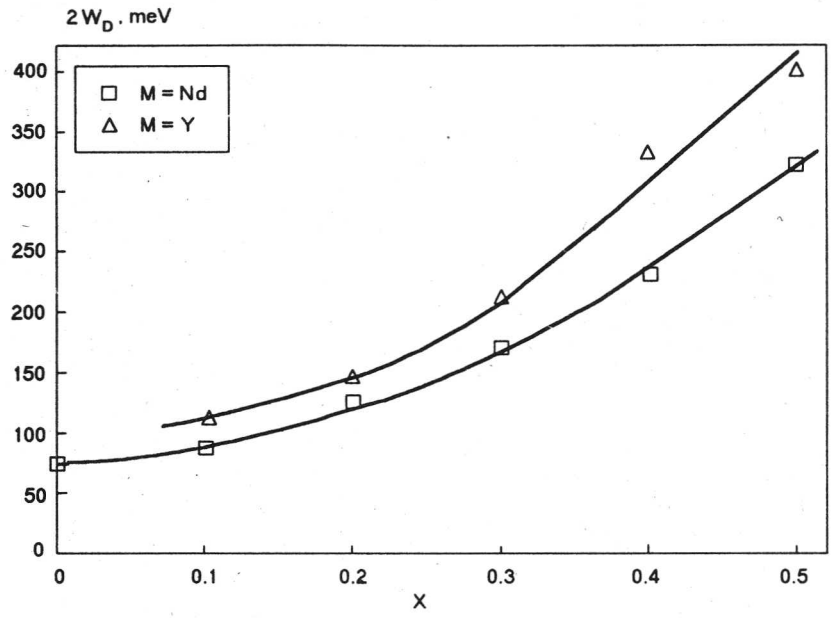
Table 2. The band spectrum parameters for $Bi_2Sr_2Ca_{1-x}M_xCu_2O_y$.

x	F	$2W_D$, meV	$2W_\sigma$, meV	C	b
M = Nd					
0.0	0.472	75	30	0.4	-0.030
0.1	0.4762	87	31	0.35	-0.028
0.2	0.4929	125	35	0.28	-0.019
0.3	0.503	170	37	0.22	-0.014
0.4	0.5168	230	45	0.195	-0.010
0.5	0.527	320	56	0.175	-0.007
M = Y					
0.1	0.4462	115	33	0.29	-0.057
0.2	0.4637	135	36	0.25	-0.050
0.3	0.4864	210	38	0.18	-0.033
0.4	0.509	325	52	0.16	-0.021
0.5	0.52	400	56	0.14	-0.017

The parameters values determined for undoped samples of both 2212 and 2223 systems, and for doped 2212–samples are presented in Tables. The analysis and comparison of these data together with Figs. 5,6 give grounds to the following conclusions.

1. The narrow band model can be used successfully to explain uncommon behavior of the transport coefficients in 2212 and 2223 Bi–based superconductors as well as in Y–Ba–Cu–O systems. Some literature data permit one to believe that band narrowness is the common feature of all known high-T_c metalloxides of copper.

2. The analysis of transport-coefficients temperature dependencies (primarily $S(T)$) on the basis of this model enables one to evaluate the band width and to draw some conclusions on the band structure (band asymmetry, for example) and on electron kinetics peculiarities (from W_σ / W_D –ratio).



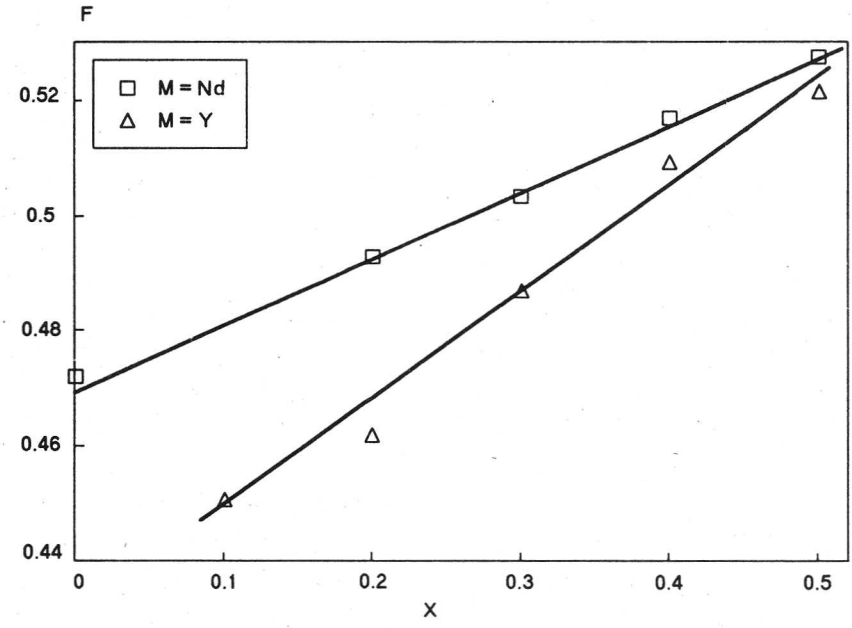


Fig. 5. Band width vs dopant content in $Bi_2Sr_2Ca_{1-x}M_xCu_2O_y$

Fig. 6. Band filling degree with electrons vs dopant content in $Bi_2Sr_2Ca_{1-x}M_xCu_2O_y$

3. As for Y-systems, the band width of both 2212 and 2223 phases of Bi-systems is of the order of 10^{-1} eV for the samples of compositions near the stoichiometry. The partial substitution of Ca by Nd or Y leads not only to decrease of the hole density, but also the band broadening.

4. Increase of the band width is accompanied by simultaneous reduction of W_σ / W_D ratio. Therefore, we could assume that increase of dopant content leads to the growth of the difference between the energy dependencies $D(E)$ and $\sigma(E)$. As a consequence, the W_σ / W_D ratio changes. One of possible reason both of band broadening and W_σ / W_D reduction may be the Anderson's localization caused by the rise of disorder.

5. Reduction of the density of states caused by the band broadening may be one of the factors (perhaps, the main factor) leading to decrease of T_c value (compare Fig. 1 with Fig. 6).

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