Scaling of the thermoelectric power in a wide temperature range in $Bi_2Sr_2Ca_{1-x}Nd_xCu_2O_y$ (x=0–0.5): Experiment and interpretation

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We report measurements of the thermopower (S) in the temperature range from T_c up to 1000 K, as well as of the resistivity and the Hall coefficient for temperatures up to T=300 K of single-phase $Bi_2Sr_2Ca_{1-x}Nd_xCu_2O_y$ compounds with $0 \leqslant x \leqslant 0.5$. It was found that the $S(T)$ dependences in the normal state have three regions of different thermopower behavior. In the first region, at low temperature (T<100–220 K), the $S(T)$ curves have a smooth maximum, which shifts to higher temperature as x increases. Then, as the temperature increases, there is an extended second region where S decreases nearly linearly with T. Finally, in the third region, at high temperature (T>620 K), the thermopower demonstrates a temperature-independent behavior for all the investigated samples. The temperature of the crossover from the second $S(T)$ region to the third one is unchanged with x. The results are discussed in the framework of a phenomenological band spectrum model.

I. INTRODUCTION

The specific features of the band structure in the normal state is one of the most important and extensively discussed problems in the physics of the high-T_c superconductors (HTSC). Reliable information on this subject would be very useful to understand the possible reason for the high critical temperature in these materials. Different approaches, both theoretical and experimental, are used to study the band structure. However, it should be noted that this problem is still unsolved.

One could expect some nonordinary specific features of the electron spectrum in the vicinity of the Fermi level. One of the reasons for this conclusion is the unusual behavior of the electron transport properties in the normal state. The temperature dependence of the resistivity, $\rho(T)$, for the samples with an optimum doping level for the different families of HTSC is linear in a wide temperature range with $\rho(0)=0$.[1] The Hall coefficient R_H rapidly drops with the temperature increase: $R_H(T) \propto 1/T$.[1,2] Thermopower value S depends considerably on Hall carriers density. But what is quite unusual is the very weak dependence $S(T)$ at high temperature (T >200–300 K) in the $YBa_2Cu_3O_y$ system (Y-123).[3–6] Various explanations of the latter phenomenon have been proposed including both single[4,6,8] and two-band[9,10] pictures, taking into account the presence of a Van Hove singularity near the Fermi level.[11]

It was shown in our previous publications that all the features of $\rho(T)$, $S(T)$, and $R_H(T)$, for the Y-123 system in the normal phase could be explained and described quantitatively on the basis of a band spectrum model that supposes the existence of a narrow peak in the electronic density of states (DOS) close to the Fermi level.[12–16] This approach and the formulas for the transport coefficients calculation were presented in Ref. 12. With this analysis, we are able to determine some band spectrum parameters by a quantitative comparison of the experimental and calculated temperature dependences of the thermopower. We have analyzed these parameters dependences on the samples composition (various oxygen content[13,17] and different cations substitutions[14–17]), and made some conclusions about the conductive band transformations. In addition, we have observed a correlation between the band spectrum parameters change and T_c value, under the different deviations from the stoichiometric composition.

The objective of the present work is to test the validity of our model for Bi-based HTSC. We focus the discussion on the thermopower behavior in a wide temperature range. First, $S(T)$ dependences of the Bi system differ essentially from those of Y-123 due to the absence of the temperature-independent region up to T=300 K.[18–21] However, it is this temperature-independent behavior of S that points to the existence of a narrow band. Therefore, it is not clear whether $S(T)$ of Bi-based HTSC can be explained within a narrow-band model. Second, the experimental data concerning a thermopower behavior at T>300 K for this HTSC system are practically absent, although it can be quite informative for the band spectrum study.

It is known that the 2212 phase of the Bi system is more stable compared to the 2223 phase. It gives us the possibility to prepare heavily doped single-phase samples and to vary the Fermi-level position over a wide range of energy using nonisovalent substitution for Ca by different rare-earth elements, R. As a result, a shift of the Fermi level and possible transformations of the band spectrum exert an effect on the transport coefficients behavior. The study of such samples with different composition appears to be a fruitful way of understanding the mechanism of electron transport in HTSC. Indeed, the $Bi_2Sr_2Ca_{1-x}R_xCu_2O_y$ system has been repeatedly investigated by many authors using different techniques,[22–27] including thermopower measurements up to $T=300$ K for samples with substitution of Y for Ca.[18,28,29]

For the above-mentioned reasons, we have chosen for our investigation $Bi_2Sr_2Ca_{1-x}Nd_xCu_2O_y$ samples with $0\leqslant x\leqslant 0.5$. We have measured the thermopower from T_c up to 1000 K, as well as the resistivity and the Hall coefficient between T_c and 300 K. The results are discussed in the framework of a narrow-band model.

II. EXPERIMENT

The ceramic samples were prepared by the standard solid-state powder processing technique from high-purity Bi, Y, and Cu oxides, and Sr and Ca carbonates. The powders were dried and pressed into pellets. The samples were calcined at $T=750$ °C for 15 h, reground and sintered at $T=850$ °C for 40 h, and then reground and sintered again at $T=860$ °C for 40 h in air. The homogeneity of the samples and the absence of the foreign phases were controlled by x-ray analysis and magnetic-susceptibility measurements.

The resistivity was measured by the standard four-probe low-frequency ac (20 Hz) method. The Hall measurements were carried out in a dc magnetic field of 1.5 T using a lock-in amplifier synchronized at 15 Hz with an alternating current of 200 mA. For the thermopower measurements, the sample was kept between two platinum electrodes, and one of them was heated. The temperature was varied by slowly introducing the sample into a liquid-helium cryostat (for the temperature range $T=T_c$–300 K), or by using a specially constructed furnace (for $T=300$–1000 K). The temperature of the hot and cold ends of the sample was measured by two Chromel-Constantan thermocouples. The temperature difference between the two ends of the sample was kept around 3–4 K throughout the measured temperature range. The absolute thermopower was calculated by correcting for the thermopower of platinum. The measurements were carried out both in the heating regime and in the cooling one. The speed of cooling or heating was about 2–5 K/min. All the measurements of the thermopower were carried out in air.

III. RESULTS

Some results of the resistivity and the Hall coefficient measurements, as well as the critical temperature, T_c, defined as the midpoint of the resistive superconducting transition, are presented in Table I. The behavior of both the resistivity and the Hall coefficient shows the usual features which are characteristic of the investigated system.[1,2] The $\rho(T)$ dependences are linear in the temperature range measured. The Hall coefficient increases with decreasing temperature, but this increase is weaker than for Y-based HTSC. In our measurements R_H increases by 20–30 % as temperature decreases from 300 to 100 K. The substitution of trivalent Nd for divalent Ca results in the increase of the absolute values of ρ and R_H, as well as the rise of the residual resistivity, ρ_0, obtained by the extrapolation of the $\rho(T)$ curves at $T=0$ K (see Table I). All these results are in a quite reasonable agreement with the literature data both for ceramic and for single-crystal samples of $Bi_2Sr_2Ca_{1-x}R_xCu_2O_y$ system.[1,2,24,28,30] T_c has a maximum near $x=0.1$, changes weakly up to $x=0.3$ and decreases rapidly with further increase in x. It should be noted that, in contrast to the critical temperature, the inverse Hall coefficient (the Hall concentration of the charge carriers) decreases monotonously with increasing x over the all Nd content range.

TABLE I. Several normal-state properties and superconducting transition temperature in the system $Bi_2Sr_2Ca_{1-x}Nd_xCu_2O_y$.

x	ρ (300 K) (mΩ cm)	ρ (300 K)/ ρ(100 K)	ρ_0 (mΩ cm)	R_H (300 K) (10^{-3} cm^3/C)	T_c (K)
0.0	1.2	2.00	0.3	1.9	76.6
0.1	2.7	1.98	0.8	2.9	83.9
0.2	3.0	1.50	1.5	4.2	82.6
0.3	3.5	1.21	2.6	6.8	75.9
0.4	3.8	1.09	3.4	9.6	56.0
0.5	11.1	1.01	9.0	12.5	36.0

As already noted, the main purpose of this paper is the investigation of the thermopower temperature dependences. The results of our S versus T measurements are shown in Fig. 1. It is necessary to note that we have made several measurements for each sample and the curves of Fig. 1 have been reproduced several times under the "heating-cooling" cycles over the temperature range $T=T_c$–1000 K. In addition, the resistivity measurements at $T=T_c$–300 K were repeated after the thermopower ones, and all the data presented in Table I have remained the same. It is clearly shown that Bi-2212 HTSC system is more oxygen stable as compared to Y-123. It is well known that, in the latter, the oxygen deficit increases rapidly due to heating in air above $T=600$–800 K. This loss of oxygen leads to an increase of the thermopower value. As a result, the $S(T)$ dependences of Y-123 measured in air become nonreproducible for cycling measurements over a high-temperature range.[31–33]

The thermopower value of $Bi_2Sr_2Ca_{1-x}Nd_xCu_2O_y$ in-

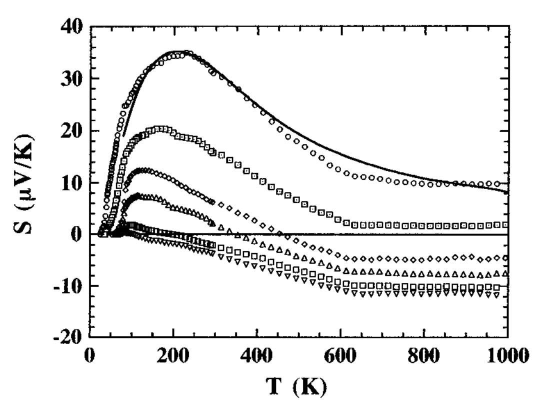

FIG. 1. Absolute thermopower vs temperature for $Bi_2Sr_2Ca_{1-x}Nd_xCu_2O_y$ samples. The Nd contents x are (in the order of increasing thermopower) 0, 0.1, 0.2, 0.3, 0.4, and 0.5. The different symbols are shown the experimental results, the solid line is the best-fitted curve for the sample with $x=0.5$ corresponding to Eq. (2).

creases with x. This fact points to the increase of the band filling with electrons, in accordance with the higher substituting element valence (Nd^{3+} replaces Ca^{2+}). It can be clearly seen in Fig. 1, that the $S(T)$ dependences in the normal states have three characteristic regions with different thermopower behavior. In the first one (from T_c to 120–200 K, depending on the Nd content) the $S(T)$ dependences have a smooth maximum, more and more pronounced and shifted to higher temperature with increasing x, in agreement with the data of Refs. 18, 28, and 29 for the substitution of Y for Ca. In fact, the thermopower behavior in this region, including the $S(T)$ variation with x, is analogous to the one of Y-123 with decreasing oxygen content or doping by nonisovalent impurities.[3,5–9,13–17] From $T=120$–200 K up to 620 K (the second region), the thermopower decreases nearly linearly with temperature. This is a well-known specific feature of the Bi system compared to Y-123. It should be noted that a similar kind of $S(T)$ behavior in the temperature region up to $T=300$ K has also been observed for the other HTSC systems such as Nd-,[34,35] Tl-,[21,36,37] and Hg-based[38–40] ones. Based on these observations and the results of their own measurements of the thermopower anisotropy in the *ab* plane of untwinned $YBa_2Cu_3O_y$, Cohn *et al.*[41] concluded that the thermopower constancy of Y-based HTSC can be explained by the existence of a very narrow band which predominates in transport along the CuO chains. On the other hand, they suggested that the linear decrease of S with increasing temperature is a common thermopower behavior of the different HTSC systems associated with the CuO_2 plane. Nevertheless, it can be clearly seen in Fig. 1, that for all our Bi-2212 samples the thermopower constancy has been observed at $T>620$ K [the third region of the $S(T)$ curves] in spite of the absence of CuO chains in this HTSC system. It means that this temperature-independent behavior of the thermopower at high temperature is a common feature of both the Y-123 and the Bi-2212 HTSC systems. Consequently, in contrast to Ref. 41, this phenomenon cannot be explained by electron transport along a narrow band which is associated with CuO chains. According to our data, the thermopower of Bi-2212 at $T>620$ K also demonstrates the canonical narrow-band behavior. Thus, we believe that our results provide strong support for the existence of a narrow band not only in Y-123, but also in Bi-2212 HTSC. In this connection, we would like to note that Takahashi *et al.*[23] by inverse photoemission, Sato, Horiba, and Nagasaka[26] by transmission spectroscopy and some other authors, also confirmed the existence of a narrow conductive band in the Bi-2212 HTSC.

Before analyzing the results obtained, one more fact should be noted. This is the quite drastic transition from the second region of $S(T)$ dependences to the third one which occurs at $T=620$ K, independently on the Nd content. It can be mentioned that we have earlier observed the analogous point of a drastic transition at a constant temperature from one type of the $S(T)$ behavior to another one in $YBa_2Cu_3O_y$ with different oxygen content.[33] Although the temperature of this transition was significantly lower ($T=350$ K), it seems that the existence of such a point can be a common feature of the different types of the HTSC materials.

IV. DISCUSSION

As already noted, the approach used in the present work is founded on the assumption that a sharp peak in the DOS exists in the band spectrum of the HTSC materials. Analogous assumption was repeatedly used, in its different aspects, to explain the specific features of the transport properties of $YBa_2Cu_3O_y$ system with different oxygen content.[4,7–9,42] Fisher and co-workers[6,43] used a narrow-band model to interpret qualitatively the thermopower and resistivity measurements in $YBa_2Cu_3O_y$ samples with some cations substitutions. In the main, much of the discussion in these papers is centered around the $\rho(T)$ linearity and the $S(T)$ constancy at high temperature, which are characteristic of the narrow-band limit. In Ref. 24 a narrow-band model has been used to describe the crossover from insulating to metallic resistivity in the case of $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_y$, but without any comparison with thermopower data. The characteristic of our approach is the possibility to describe of not only qualitatively, but also quantitatively, the $S(T)$ dependences in the whole temperature range above T_c. As a result, we can determine some parameters of the band structure by comparison of the experimental and calculated thermopower temperature dependences. Besides, it is possible to describe qualitatively the $\rho(T)$ and $R_H(T)$ dependences using the same values of the parameters of this model.[17]

Details of our approach have been published in Ref. 17. Here, we would like to describe briefly only the main points of our model and, accordingly, some results of the transport properties of Y-123 HTSC analysis. As shown in Ref. 17, if the Fermi level ε_f is located in the region of a sharp peak of the DOS function, it is its narrowness that determines the specific features of the transport coefficient behavior. It should be noted that we do not discuss the nature and origin of this peak. It can be either a single narrow band or a sharp DOS peak on a wide band background. In the last case, if the DOS inside the peak is significantly greater than outside, the normal-state electron transport will also be determined by the structure and properties of this peak. If so, the existence of a Van Hove singularity near the Fermi level can be considered as the most probable reason for this peak origin. The possibility of the so-called Van Hove scenario in HTSC is under extensive experimental and theoretical study now. This approach is used not only for the description of different properties (including the transport ones, see Ref. 11), but also for the explanation of the high superconducting transition temperature.[44] In this connection, our results of the transport coefficients analysis can be considered as a support for the plausibility of this scenario. For simplicity, we will use below the term "narrow band" for both mentioned cases.

Our model includes three phenomenological parameters. The first of them is the degree of band filling with electrons F, which is equal to the ratio of the number of electrons to the total number of states in the band. The F value determines the sign and the value of the thermopower in the high-temperature limit ($k_BT>W$, where W is the bandwidth, k_B is Boltzmann constant). In this limit, the temperature-independent thermopower is given by

$$S=\frac{k_B}{e}\ \ln\frac{F}{1-F}. \tag{1}$$

As shown in Ref. 17, the band narrowness gives the possibility to use the simplest approximations for the DOS, $N(\varepsilon)$, and the differential conductivity, $\sigma(\varepsilon)$, by rectangles of different width. This approximation makes it possible to derive analytical expressions for the temperature dependences of the transport coefficients using three fitting parameters. They are the band filling F, the total effective bandwidth W_D, and the effective width of an energy interval of the electrons which give the main contribution to the electrical conduction process, W_σ (i.e., the "conductivity" effective bandwidth).

In the framework of this approximation, the expression for the thermopower can be written in the following form:

$$S=-\frac{k_B}{e}\left\{\frac{W_\sigma^*}{\sinh W_\sigma^*}\left[e^{-\mu^*}+\cosh W_\sigma^*-\frac{1}{W_\sigma^*}\right.\right.$$
$$\left.\left.\times(\cosh\mu^*+\cosh W_\sigma^*)\ln\frac{e^{\mu^*}+e^{W_\sigma^*}}{e^{\mu^*}+e^{-W_\sigma^*}}\right]-\mu^*\right\}, \quad (2)$$

where

$$\mu^*\equiv\mu/k_BT=\ln\frac{\sinh(FW_D^*)}{\sinh[(1-F)W_D^*]}, \quad (3)$$

μ is the chemical potential, $W_D^*\equiv W_D/2k_BT$, $W_\sigma^*\equiv W_\sigma/2k_BT$.

It should be noted that we use only three fitting parameters which are assumed to be temperature independent. Nevertheless, as one can see in Refs. 13, 17, and 45, there is a good agreement between the experimental and calculated temperature dependences for all the transport coefficients. This fact can be considered as an additional argument in favor of our model.

According to our previous results for Y-based HTSC, the W_D and W_σ values are different. This may be due to a different nature of energy dependences of the $N(\varepsilon)$ and $\sigma(\varepsilon)$ function. At the same time, taking into account the variations of W_D and W_σ with the oxygen deficit and the substituting elements content, we came to conclusion[13] that the most probable reason for the W_σ/W_D ratio change, under deviations from stoichiometry, appears to be the Anderson localization of the states at the band edges caused by lattice disordering.[46] If so, the decrease of the W_σ/W_D ratio can be considered as an evidence for the increase of the degree of localization. Thus, analyzing the changes of the model parameters we can get some information on peculiarities of kinetics, dynamics, and scattering of the charge carriers. Besides, we have observed a correlation between the band-structure parameters and the T_c value in the samples with different substitutions.[13–17] The deviation from the stoichiometry in $YBa_2Cu_3O_y$ causes a band broadening (W_D value increases) and also a Fermi-level shift from the band center. Both of these effects lead to the reduction of the $N(\varepsilon_F)$ value. The latter is believed to be the major reason for the T_c decrease.

We now turn to the results obtained for the $Bi_2Sr_2Ca_{1-x}Nd_xCu_2O_y$ samples. Obviously, in order to interpret the $S(T)$ specific features of Bi-based HTSC in the framework of the same narrow-band model we have to make an additional assumption. It is necessary to note that Eq. (2) is valid, if we assume the narrow band to be symmetric. Our previous results have shown this condition to be satisfied for Y-123 system. In the case of the Bi-based HTSC, we suggest that there is a slight asymmetry of the band. The simplest method to take this into account is the introduction of some distance (bW_D, where b is the asymmetry parameter) between the $N(\varepsilon)$ and $\sigma(\varepsilon)$ rectangles centers. If so, Eq. (2) still remains valid, if we replace μ, calculated from Eq. (3), by $\mu-bW_D$.

Using this approach, we are able to describe quantitatively the temperature dependences of the thermopower for the investigated samples. To determine the parameters of our model, we have fitted the experimental $S(T)$ dependences with the calculated ones to achieve the best agreement "by eye" in the whole temperature range above T_c. One should note, that the different parameters affect different specific features of the $S(T)$ dependence (details of this influence can be found in Ref. 17). As a result, it is possible to determine the values of the all parameters quite unambiguously. According to our calculations, the possible error can be estimated as ±0.003 for F and $\pm10\%$ of magnitude for W_D and W_σ. Thus, it gives a well-grounded possibility to discuss the evolution of these parameters with the change of the sample composition.

As an example, the best-fitted $S(T)$ curve for the sample with $x=0.5$ is shown by the solid line in Fig. 1. It is seen to be in quite reasonable agreement with the experimental data. Certainly, the "rectangular" approximation for $N(\varepsilon)$ and $\sigma(\varepsilon)$ is very simple and quite crude. As a result, the calculated dependences of the thermopower are smooth. They do not demonstrate the drastic transition from the second to the third region of the $S(T)$ curves which we have observed experimentally. It seems to be necessary for the best agreement to take into account the band-structure features in more detail. A more realistic analysis should consider the possible temperature dependence of the band spectrum parameters when we deal with a wide temperature range. Nevertheless, we believe that these present results make it possible to conclude that the narrow-band model can be successfully used for the Bi-based HTSC. Besides, it is necessary to note that the calculated $\rho(T)$ and $R_H(T)$ dependences retain all their characteristic features in the framework of an asymmetric model and are in good qualitative agreement with the experimental results. In addition, taking into account a band asymmetry, it is possible to explain the opposite sign of the thermopower and the Hall coefficient observed for the Bi-based HTSC.

Figure 2 shows the calculated F and W_D values as function of the Nd content. The form of these dependences is very similar to those we observed in substituted $YBa_2Cu_3O_y$ with different deviations from stoichiometry.[13–17] The increase of the Nd content in $Bi_2Sr_2Ca_{1-x}Nd_xCu_2O_y$ leads to increasing value of F (the hole density decreases in accordance with a higher valence of Nd compared to Ca) and to a significant transformation of the band.

Note, that the band filling is nonlinear in the Nd content. The $F(x)$ dependence shows an increase of its curvature as x increases. To explain this fact, it is necessary to take into account the possible nature of the band in this material. This question is under intensive investigation, both theoretically[47–50] and experimentally.[24,26–27] There are different explanations for the consequences of the doping of the antiferromagnetic insulator $Bi_2Sr_2RCu_2O_y$ by Ca. Nevertheless, most of the authors suggests that the new states appear

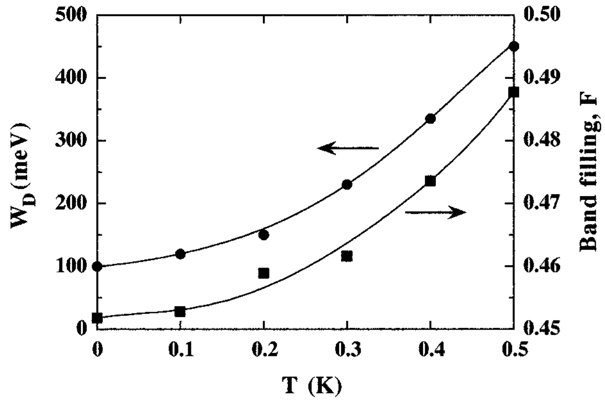

FIG. 2. The total effective bandwidth and the degree of band filling vs Nd content for $Bi_2Sr_2Ca_{1-x}Nd_xCu_2O_y$.

in the vicinity of the Fermi level and, therefore, a narrow band is immediately formed upon hole doping. The question is whether the band is formed by the so-called ‘‘midgap’’ impurity states (similar to the case of doped semiconductors) or by a transfer of states from the upper band to the lower one due to strong correlation effects. Although this is a schematic picture only, the important feature is the rise of the number of states in the band with increasing Ca content. If so, there are two reasons for the increase of F with x in the $Bi_2Sr_2Ca_{1-x}Nd_xCu_2O_y$ samples: the increase of the number of electrons (which should be linear in x) and, at the same time, the decrease of the number of states in the band. It is clear, that in this case the $F(x)$ dependence should be nonlinear, and its curvature should increase with x. In this connection, our results seem to be quite reasonable.

The total effective bandwidth increases gradually with x. At the same time, this effect is accompanied by an insignificant increase of W_σ (from W_σ=40 meV to W_σ=65 meV when x runs from 0 to 0.5), i.e., the W_σ/W_D ratio gradually and strongly decreases with increasing x. Thus, the transformation of the band occurs mainly through an enlargement of the region of localized states near the band edges. Therefore, we can assume that the effect of the lattice disordering is of great importance in the case of Bi-based HTSC. The rise of the disorder with increasing impurity content causes a localization of the states at the band edges and a broadening of the band which are in a good agreement with the Anderson localization. On the other hand, the increase of the effective bandwidth leads to a decrease of the $N(\varepsilon_F)$ value, which can be considered as the main reason for the reduction of T_c. Thus, the correlation between the band spectrum parameters and the critical temperature revealed earlier for the Y-123 system is observed also in the case of Bi-2212 HTSC.

It can be noted also, that the values of the effective bandwidth obtained for the investigated system are close to those of Y-123 (see our results in Refs. 13–17). Besides, the results obtained are in quite reasonable agreement with data of Ref. 26, whose authors suggest a bandwidth in $Bi_2Sr_2Ca_{1-x}Nd_xCu_2O_y$, with x=0.4–1.0, to be around or less than 650 meV. As for the band asymmetry, our calculations show that it is quite slight. The relative energy shift of the $N(\varepsilon)$ and $\sigma(\varepsilon)$ rectangles centers is about 3–5 % of the total effective corresponding bandwidth.

Thus, the values of the band spectrum parameters, their changes under influence of deviations from stoichiometry and the possible explanation of these changes are analogous for Y-123 and Bi-2212 HTSC. As a consequence, these results clearly demonstrate the similarity of the main properties of the charge carriers system in these two types of the HTSC materials.

V. CONCLUSION

In summary, we have studied the thermoelectric power of the $Bi_2Sr_2Ca_{1-x}Nd_xCu_2O_y$ (x=0–0.5) compounds in a wide temperature range from T_c to 1000 K. It was found that the region of the linear decrease of the thermopower with temperature extends up to T=620 K. Above this temperature, the thermopower is temperature independent for all the investigated samples.

The temperature-independent behavior of the thermopower at high temperature provides strong support for the existence of a narrow conductive band in the band spectrum of Bi-based HTSC. The asymmetric narrow-band model can be successfully used for the explanation of the transport properties of the Nd-doped Bi-2212 HTSC, including the quantitative description of the thermopower in the whole temperature range measured. The analysis of the experimental results shows that the main feature of the band spectrum and the nature of its transformation (under the deviation from the stoichiometric composition) are analogous for Y- and Bi-based HTSC.

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