Normal-state Nernst coefficient in high-temperature superconductors of the Y-Ba-Cu-O system

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Abstract. A comparative experimental study of the normal-state Nernst coefficient, Q, in high-temperature superconductors of the $YBa_2Cu_3O_y$ system with different types of deviations from the stoichiometry was performed. The peculiarities of the $Q(T)$ dependences characteristic of Y-based HTSC, as well as the specific features of the influence of different types of doping on the absolute Q value were revealed. The obtained $Q(T)$ dependences were analyzed on the basis of a narrow-band model together with the thermopower temperature dependences measured on the same samples. It is shown that the developed approach allows one to describe quantitatively all the experimental Nernst results and to determine from their analysis the values of the charge-carrier mobility and the degree of the dispersion law asymmetry. The data on the variation of these parameters under influence of different types of doping are obtained and discussed with respect to the modification of the energy spectrum structure induced by studied dopants.

1. Introduction

Besides anomalously high values of the critical temperature, T_c, high-temperature superconductors (HTSC) are well-known to be characterized by unusual properties in the normal (non-superconducting) state. One of the examples is the behavior of the transport coefficients, whose temperature and concentration dependences demonstrate some peculiarities in comparison with those of the standard objects of the solid state physics, such as metals and semiconductors. Obviously, this is related to the specific features of the normal-state band spectrum structure, but questions on its main parameters and the mechanisms of its modification under doping, as well as on parameters of the charge-carrier system are still under discussion. This is why a lot of models based of different and even mutually exclusive assumptions were proposed to describe the electron transport phenomena in HTSC [1-7].

Note that despite a huge number of the experimental results devoted to an analysis of the temperature dependences of the resistivity, ρ, thermopower, S, and Hall coefficient collected already in the earlier years of studying the HTSC-materials (see, for example, reviews [8-10] and references therein), the data on the behavior of the Nernst coefficient, Q, at $T > T_c$ are limited in number, although this coefficient, according to the classical theory of the electron transport, is quite informative, especially in case of polycrystalline samples. The main reason for this is the fact that the quantitative analysis of the $Q(T)$ dependences cannot be performed when one uses a model-independent approach. Besides, to obtain the reliable information from such an analysis it is necessary to discuss the experimental Nernst data together with the results on other transport coefficients in the

framework of a unified model concept on the energy spectrum structure in a studied material. Such an approach can be realized on the basis of the narrow-band model [7] allowing one to perform the joint quantitative analysis of the $S(T)$ and $Q(T)$ dependences measured on the same samples [11, 12].

For the above reasons, this paper is devoted to the comparative experimental study of the Nernst coefficient in yttrium-based HTSC samples with different types of doping and quantitative analysis of the obtained results together with the thermopower data.

2. Samples and Experimental Details

The samples of $YBa_2Cu_3O_{7-x}$ ($x = 0.09$-0.52), $YBa_2Cu_{3-x}Zn_xO_y$ ($x = 0.05$-0.12), $Y_{1-x}Ca_xBa_2Cu_3O_y$ ($x = 0.05$-0.2), $Y_{1-x}Ca_xBa_{1.5}La_{0.5}Cu_3O_y$ ($x = 0.2$-0.4), and $Y_{1-x}Ca_xBa_{2-x}La_xCu_3O_y$ ($x = 0.0$-0.5) were used for investigations. Such compositions were chosen for a comparative analysis because in these cases increasing doping level influences the critical temperature and transport coefficients values in different ways that should make it possible to trace the Nernst coefficient variations under different types of changes in the band spectrum and charge-carrier system parameters. Ceramic samples were prepared by the standard solid-state processing technique from the high-purity oxides and carbonates mixed in the required proportions. The oxygen deficit in $YBa_2Cu_3O_{7-x}$ was created by an annealing of the initial sample in vacuum at different temperatures for 2 h, for samples with cation doping the final oxygen saturation was not performed. In case of the $Y_{1-x}Ca_xBa_2Cu_3O_y$ system we used the samples characterized by an oxygen deficit created by an annealing in vacuum at 450 °C for 2 h. X-ray diffraction analysis has shown all the samples to be almost of single phase with amount of foreign impurities not exceeding 1-2%. The sample homogeneity was controlled by measuring the local values of the thermopower in various points on the sample surface at room temperature.

The $\rho(T)$ dependences were measured by the standard four-probe low-frequency ac ($f = 20$ Hz) method. The thermopower was measured by a differential method relative to copper electrodes at the temperature difference between the two ends of a sample of about 2 K and then calculated by correcting for the absolute thermopower of copper. The Nernst coefficient was measured in a constant magnetic field of 1.8 T. We used thin samples of about 1 mm in the ∇T direction to increase the Nernst signal and a reversible magnetic field to exclude a contribution of even magnetic effects to the measured Nernst voltage. Details of the Nernst coefficient measurements can be found elsewhere [12]. The resistivity and thermopower were measured in the temperature range $T = T_c$–300 K, the Nernst coefficient was measured at $T = 77$–310 K. The absolute error in determining the Nernst coefficient values when measuring the $Q(T)$ dependences did not exceed 10 %, the minimal securely fixed Q value at $T = 300$ K in the mobility units was about $5 \cdot 10^{-3}$ cm^2/(V·s).
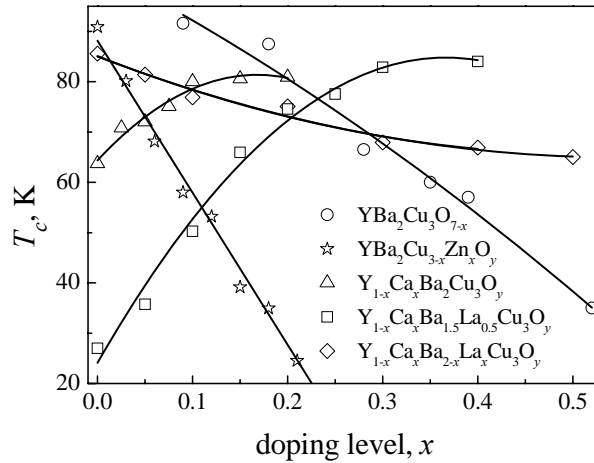
3. Experimental Results

The critical temperature values for all the studied samples determined as a midpoint of the resistive superconducting transition are shown in figure 1. One can see that the T_c value changes with doping in various ways. In the $YBa_2Cu_3O_{7-x}$, $YBa_2Cu_{3-x}Zn_xO_y$, and $Y_{1-x}Ca_xBa_{2-x}La_xCu_3O_y$ systems, T_c decreases, but at different rates, whereas in the $Y_{1-x}Ca_xBa_2Cu_3O_y$ and $Y_{1-x}Ca_xBa_{1.5}La_{0.5}Cu_3O_y$ systems increasing calcium content leads to a T_c rise. The physical reasons for a T_c restoration in two last cases were earlier discussed elsewhere [13, 14].
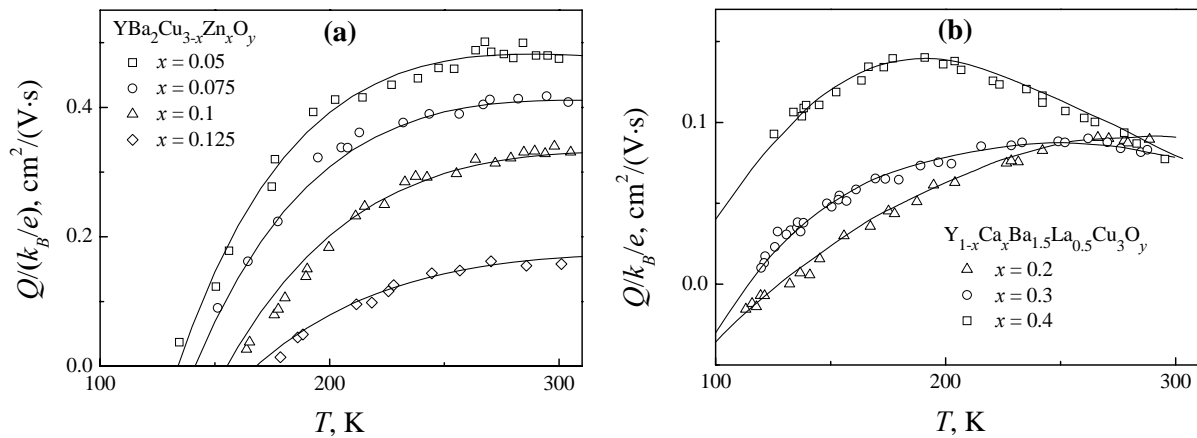
The thermopower temperature dependences demonstrate all the well-known peculiarities typical for yttrium-based HTSC including some specific features characteristic of calcium-containing samples [13]. A detailed description and analysis of the thermopower results can be found in our earlier papers [13-16]. For this reason we will focus here on the experimental Nernst results.

For all the studied samples a character of the $Q(T)$ dependence remains qualitatively unchanged. As examples, figure 2 presents the experimental results for two of these systems, namely, $YBa_2Cu_{3-x}Zn_xO_y$ and $Y_{1-x}Ca_xBa_{1.5}La_{0.5}Cu_3O_y$. One can see that the Nernst coefficient is positive at $T = 300$ K and its values are extremely small (they do not exceed 1 cm^2/(V·s) in the mobility units for all the doping types and ranges, see figure 3). As the temperature decreases, the Q value increases slightly, then the $Q(T)$ dependence demonstrates a broad maximum followed by a sharp fall of the Q value.
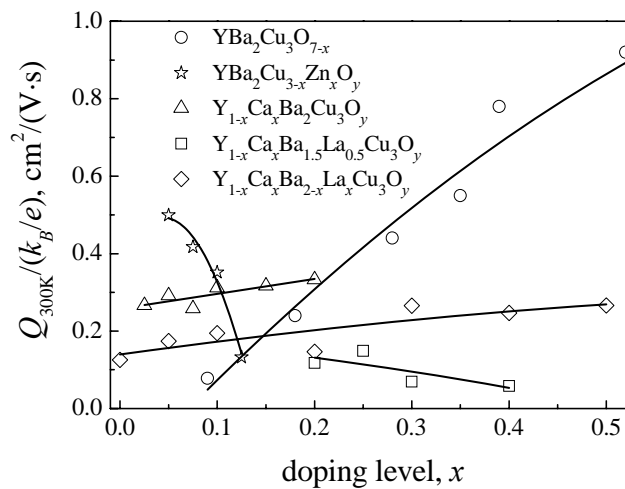
Additionally, in the $Y_{1-x}Ca_xBa_{2-x}La_xCu_3O_y$ samples with $x = 0.2$ and $x = 0.3$, a transition to negative Q values is observed at $T < 150$ K.

Figure 1. Critical temperature vs doping level

Figure 2. Nernst coefficient vs temperature for $YBa_2Cu_{3-x}Zn_xO_y$ (a) and $Y_{1-x}Ca_xBa_{1.5}La_{0.5}Cu_3O_y$ (b) samples. Symbols present the experimental data, lines are the calculation results
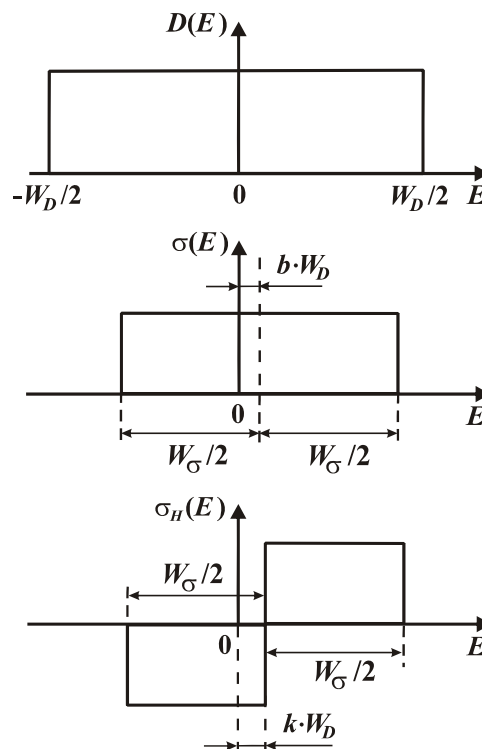

Figure 3. Nernst coefficient at $T = 300$ K vs doping level

The effect of doping level on the Nernst coefficient value at $T = 300$ K for all the systems studied is shown in figure 3. For $YBa_2Cu_3O_{7-x}$ with different oxygen content the $Q(T = 300$ K$)$ value increases almost linearly and quite significantly with increasing doping level (from 0.078 to 0.92 cm^2/(V·s) as x increases from 0.09 to 0.52). In the $Y_{1-x}Ca_xBa_2Cu_3O_y$ and $Y_{1-x}Ca_xBa_{2-x}La_xCu_3O_y$ systems, the Nernst coefficient value increases with x very slightly, while in the $YBa_2Cu_{3-x}Zn_xO_y$ and $Y_{1-x}Ca_xBa_{1.5}La_{0.5}Cu_3O_y$ systems the $Q(T = 300$ K$)$ value decreases with increasing doping level, although to varying degrees. Thus, in general there is no correlation between the doping-induced variations of the Q values, on the one hand, and values of both T_c (see figure 1) and other transport coefficients (see [13-17]), on the other hand.

3. Analysis of the experimental data and discussion

The experimental results on the Nernst coefficient were quantitatively analyzed on the basis of a narrow-band model [7, 13] together with the data on the thermopower temperature dependences obtained earlier for the same samples [13-17]. According to this model, if the band responsible for the conduction process is narrow (which means that its half-width does not exceed the values of k_BT by more than an order of magnitude, where k_B is the Boltzmann constant), the analytic expression for the transport coefficients can be obtained by using the simplest rectangular approximation for the density-of-states, $D(E)$, differential conductivity, $\sigma(E)$, and Hall conductivity, $\sigma_H(E)$ functions (see figure 4).

Figure 4. Approximations for the $D(E)$, $\sigma(E)$, $\sigma_H(E)$ functions used in the narrow-band model

It is necessary to stress that widths of rectangles approximating these functions can be different due to both a character of the energy dependence of the corresponding functions and a localization of the charge-carriers at the band edges [7, 13]. If so, the W_D value is the total effective bandwidth, W_σ is the effective width of the delocalized states interval, and the W_σ/W_D ratio characterizes the degree of state localization. Besides, these rectangles can be shifted relative to each other by the $b·W_D$ value, where b is the band asymmetry degree, in case the $D(E)$ function is asymmetric [7, 13, 14]. At last, as shown

by the theoretical analysis of the Nernst coefficient behavior in case of a narrow conduction band [11], for the correct description of the $Q(T)$ dependences in HTSC one should take into account a possible asymmetry of the dispersion law. This can be modeled by shifting the point of change in the sign of the $\sigma_H(E)$ function by the value of $k \cdot W_D$ relative to the middle of the band (see figure 4). The k parameter value thus characterizes the degree of the dispersion law asymmetry.

In doing so, using the standard kinetic integrals and the above approximations for the $D(E)$, $\sigma(E)$, $\sigma_H(E)$ functions (see figure 4), we have obtained the following expressions quantitatively describing the temperature dependences of the thermopower and Nernst coefficient [7, 11, 13]:

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

$$Q = \frac{1}{eT}u\left(\frac{I_{H_1}}{I_0} - \frac{I_{H_0}I_1}{I_0^2} \right),$$

where $\mu^* \equiv \mu/k_B T = \ln\dfrac{\sinh(FW_D^*)}{\sinh\left((1-F)W_D^*\right)} - 2bW_D^*$, $W_D^* \equiv W_D/2k_B T$, $W_\sigma^* \equiv W_\sigma/2k_B T$, μ is the

electrochemical potential, e is the elementary charge, u is the band-averaged electron mobility,

$$I_0 = \int\limits_{-W_\sigma/2+bW_D}^{W_\sigma/2+bW_D}\left(-\frac{\partial f_0}{\partial E} \right)dE, \qquad I_1 = \int\limits_{-W_\sigma/2+bW_D}^{W_\sigma/2+bW_D}\left(-\frac{\partial f_0}{\partial E} \right)E\,dE, \qquad I_{H_0} = \int\limits_{-W_\sigma/2+kW_D}^{W_\sigma/2+kW_D}\left(-\frac{\partial f_0}{\partial E} \right)\operatorname{sign}(E-kW_D)dE,$$
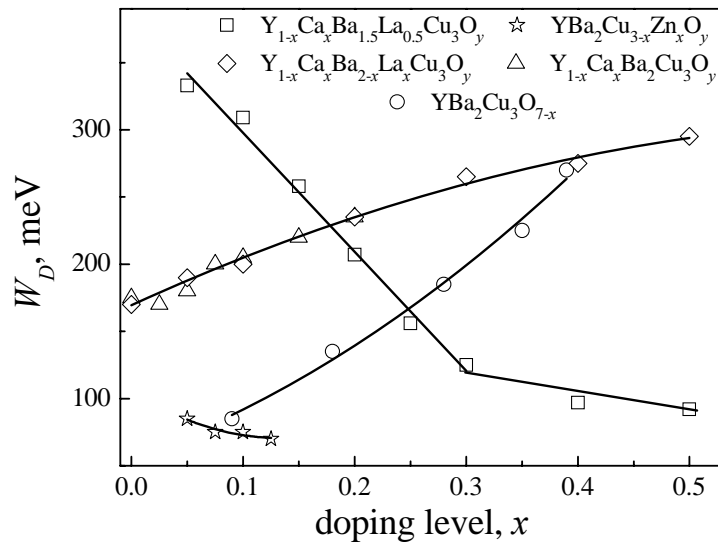
$$I_{H_1} = \int\limits_{-W_\sigma/2+kW_D}^{W_\sigma/2+kW_D}\left(-\frac{\partial f_0}{\partial E} \right)\operatorname{sign}(E-kW_D)E\,dE,\ f_0 \text{ is the Fermi-Dirac function, } F \text{ is the degree of band filling}$$

with electrons, which is equal to the ratio of the number of electrons to the total number of states in the band.
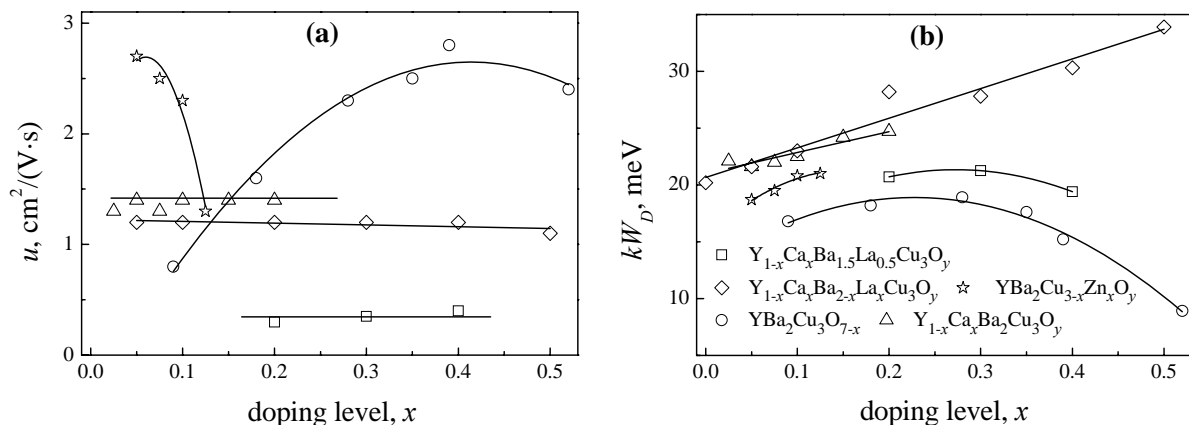
Thus, the calculated $S(T)$ and $Q(T)$ dependences are fully determined by the values of the six model parameters (W_D, W_σ, F, b, u, k), all of which have a clear physical meaning. It is important that the first four of them can be unambiguously (or, at least, with a small error) determined from the quantitative analysis of the experimental temperature dependence of the thermopower for a sample of the specific composition that was repeatedly demonstrated in our earlier publications [7, 13, 14, 16, 17]. Analyzing the experimental $Q(T)$ dependence measured for the same sample one can use these values, so that in such a case the calculated $Q(T)$ dependence is determined by the values of only two additional model parameters (u, k). Moreover, as clearly seen from the above formulae, only one parameter, k, influences a character of the temperature dependence of the Nernst coefficient, while the mobility value, u, determines the absolute Q values. All these facts essentially simplify the analysis of the experimental results making it possible to determine the u and k values from the $Q(T)$ analysis and to simultaneously specify the values of four parameters preliminary obtained from the $S(T)$ analysis. Thus, one can definitely determine the values of all six model parameters from the joint analysis of the experimental $S(T)$ and $Q(T)$ dependences.

We have used the described approach for analyzing the experimental results obtained. Results of the thermopower analysis, values of the main model parameters (W_D, W_σ, F, b) determined from this analysis, and discussion of their variations under doping can be found in [13-17]. Here we present only the summary of the results obtained for the effective bandwidth variations (see figure 5). The W_D value is seen to change with increasing doping level in different ways. The oxygen deficit in the $YBa_2Cu_3O_{7-x}$ system leads to a strong band broadening, in the $Y_{1-x}Ca_xBa_2Cu_3O_y$ and $Y_{1-x}Ca_xBa_{2-x}La_xCu_3O_y$ systems the W_D value increases rather insignificantly, in the $YBa_2Cu_{3-x}Zn_xO_y$ system it remains almost unchanged, and in the $Y_{1-x}Ca_xBa_{1.5}La_{0.5}Cu_3O_y$ system a strong narrowing of the band is observed. Thus, we have a possibility to analyze the Nernst coefficient behavior in cases of all the possible types of the energy spectrum modifications under doping.

The calculated $Q(T)$ curves for samples of the $YBa_2Cu_{3-x}Zn_xO_y$ and $Y_{1-x}Ca_xBa_{1.5}La_{0.5}Cu_3O_y$ systems are shown in figure 2 together with the experimental data. It is seen that for all the samples a good agreement between the experimental and calculated results is achieved. This fact can be considered as a powerful argument in favor of using the narrow-band model as an effective tool for the complex quantitative analysis of the electron transport phenomena in HTSC in the normal state.

Figure 5. Total effective bandwidth vs doping level

Figure 6. Variation of the electron mobility (a) and the absolute value of the energy shift of the Hall conductivity function (b) with doping level

The results obtained from the Nernst coefficient analysis are presented in figure 6. One can see that for all the studied samples the electron mobility is extremely low, its values do not exceed 3 cm²/(V·s). In our opinion, this is resulted from a large effective mass of electrons that is usually characteristic of narrow-band systems. A character of the mobility variation with doping depends strongly on a type of deviation from the stoichiometry. In the $Y_{1-x}Ca_xBa_{1.5}La_{0.5}Cu_3O_y$, $Y_{1-x}Ca_xBa_{2-x}La_xCu_3O_y$, and $Y_{1-x}Ca_xBa_2Cu_3O_y$ systems, the u value remains almost unchanged, in the $YBa_2Cu_3O_{7-x}$ system the mobility increases with oxygen deficit, in the $YBa_2Cu_{3-x}Zn_xO_y$ system its value falls sharply with increasing Zn content. To explain such a different mobility behaviour it is necessary to take into account a character of the energy spectrum modification under doping in the studied systems.

As shown in our publications devoted to the analysis of the thermopower results for different doped Y-based HTSC-systems [7, 13, 14, 16, 17] on the basis of the narrow-band model, the modification of

the energy spectrum under doping is mainly related to the Anderson localization [18] induced by a rising system disordering when introducing an impurity into the lattice or changing the oxygen content. If so, a single non-isovalent doping usually leads to an increase in both the W_σ and W_D values and simultaneously to a decrease in their ratio [7, 13]. However, in co-doped and calcium-containing systems, as well as in cases of some specific dopants, increasing impurity content can lead to additional peculiarities in a character of the conductive band modification [13, 14, 16, 17]. As already mentioned, a detailed description of the variation of the energy spectrum parameters under doping in all the studied systems is presented in our earlier publications [13-17]. Here we use these results to explain the observed changes in the charge-carrier mobility.

The mobility value is well-know to be proportional to the averaged relaxation time of carriers, but inversely proportional to their effective mass. For this reason, a broadening of the conductive band (an increase in W_σ and W_D values), leading to a decrease of the effective mass, should result in a mobility increase. On the other hand, increasing doping level induces a rise of the system disordering (a decrease in the W_σ/W_D ratio) that enhances the probability of the charge-carrier scattering and thus decreases the relaxation time value resulting in a mobility reduction. As a result, these two factors, characterizing the band spectrum modification under doping, influence the charge-carrier mobility in an opposite way. A character of the effect of a particular dopant on the u value is determined by which of these factors is prevailing in case of the studied doped system. In the $Y_{1-x}Ca_xBa_{2-x}La_xCu_3O_y$ and $Y_{1-x}Ca_xBa_2Cu_3O_y$ systems, a slight band broadening with x is accompanied by a small decrease in the W_σ/W_D ratio [13, 14, 16], i.e., a slight increase in the system disordering. In the $Y_{1-x}Ca_xBa_{1.5}La_{0.5}Cu_3O_y$ system the conductive band narrows strongly and simultaneously the degree of system disordering decreases (the W_σ/W_D ratio increases), both due to the effect of charge compensation realized in co-doped systems [13, 17]. As a result, in all these three systems, the two above effects compensate the influence of each other on the mobility value and it remains unchanged with doping. In the $YBa_2Cu_3O_{7-x}$ system the band broadens much stronger than the W_σ/W_D ratio falls [7, 13] that results in an increase in the charge-carrier mobility. In the $YBa_2Cu_{3-x}Zn_xO_y$ system, increasing Zn content leads to a slight band narrowing, but at the same time the degree of the charge localization increases strongly [13] because of destroying the conductive band [19], i.e., two factors considered above are summarized and the u value falls quite strongly. Thus, for all the studied systems the observed variation of the charge-carrier mobility can be explained by taking into account the character of the energy spectrum modification induced by the specific type of doping.

When analyzing the modification of the dispersion law (characterized in our model by the k parameter value), it is more reasonable to consider the absolute value of the energy shift of the point of changing sign of the $\sigma_H(E)$ function, $k \cdot W_D$. Dependences of this value on the doping level are presented in figure 6 (b). It is seen that, despite qualitatively different and in some cases very strong changes in the W_D value with increasing doping level (see figure 4), the $k \cdot W_D$ value varies rather insignificantly in a range from 10 to 30 meV for all the types and contents of dopants. Taking into account the small $k \cdot W_D$ values, a limited range of their variations, and a simplicity of the model used for transport coefficients analysis, one can conclude that the $k \cdot W_D$ value remains approximately unchanged in Y-based HTSC samples of varying compositions. It is also necessary to note that, in contrast to the asymmetry of the density-of-state function (characterized in our model by the b parameter), which is, in case of Y-based HTSC, characteristic of only calcium-containing samples [7, 13, 14, 16, 17], the dispersion law asymmetry is observed in all the studied samples including the calcium-free ones. Both these facts make is possible to conclude that the asymmetry of the dispersion law is not related to an effect of a specific impurity, but rather the fundamental property of the energy spectrum structure in Y-based HTSC.

4. Conclusions

Thus, this paper presents the results of the comparative study of the Nernst coefficient behaviour in the normal state for Y-based high-temperature superconductors with different types of deviations from the stoichiometry. The main peculiarities of the temperature and concentration dependences of this

coefficient are revealed and discussed. It is shown that the narrow-band model can be used for the joint quantitative analysis of the thermopower and Nernst coefficient allowing one to describe all the specific features of their temperature dependences and to determine the values of all the model parameters characterizing the energy spectrum structure and charge-carrier system properties in samples of different compositions. The values of the charge-carrier mobility for all the studied samples were determined. The mobility was found to be extremely low, its values do not exceed $3 \text{ cm}^2/(\text{V·s})$. The observed character of the mobility change with increasing doping level for all the studied systems can be explained by the energy spectrum modification occurring due to an influence of the specific type of doping. The energy spectrum structure in all the studied samples is shown to be characterized by an asymmetry of the dispersion law. The degree of this asymmetry changes with doping so that the absolute value of the energy shift of the point of changing sign of the Hall conductivity function varies slightly, being the fundamental characteristic of Y-based high-temperature superconductors.

Acknowledgments

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