

Original article

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## COMPARATIVE STUDY AND ANALYSIS OF THE THERMOPOWER AND THE NERNST COEFFICIENT IN THE $Y_{0.85}Ca_{0.15}Ba_{2-x}La_xCu_3O_y$ AND $Y_{0.85-x}Ca_{0.15}Pr_xBa_2Cu_3O_y$ SYSTEMS

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**Abstract:** In this paper, we present the experimental results on the modification of the temperature dependences of the thermopower and the Nernst coefficient in a high-temperature superconductor of the  $Y_{0.85}Ca_{0.15}Ba_2Cu_3O_y$  composition under lanthanum and praseodymium doping. We have revealed specific features of the studied impurities influence in comparison with cases of single doping which are resulted from the presence of calcium ions in the lattice. The joint quantitative analysis of the experimental temperature dependences of the transport coefficients was performed, and this allowed us to determine the values of the main energy spectrum and charge-carrier system parameters in the studied samples. We analyzed the reasons for changes in the nature of the lanthanum and praseodymium influence induced by the calcium ions' presence in the lattice and showed that they were different. The results obtained for the modification of the energy spectrum structure under doping allowed us to explain the peculiarities of the concentration dependences of the critical temperature in the systems under study.

**Keywords:** high-temperature superconductor, doping effect, critical temperature, thermopower, Nernst coefficient, energy spectrum

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Научная статья

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**СРАВНИТЕЛЬНОЕ ИССЛЕДОВАНИЕ И АНАЛИЗ  
КОЭФФИЦИЕНТОВ ТЕРМОЭДС И НЕРНСТА – ЭТТИНГСГАУЗЕНА  
В СИСТЕМАХ  $Y_{0,85}Ca_{0,15}Ba_{2-x}La_xCu_3O_y$   
И  $Y_{0,85-x}Ca_{0,15}Pr_xBa_2Cu_3O_y$**

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**Аннотация.** В работе представлены результаты экспериментального исследования модификации температурных зависимостей коэффициентов термоэдс и Нернста – Эттингсгаузена в высокотемпературном сверхпроводнике состава  $Y_{0,85}Ca_{0,15}Ba_2Cu_3O_y$  под действием легирования лантаном и празеодимом. Выявлены особенности влияния исследованных примесей, по сравнению со случаями одиночного легирования, вызванные наличием в решетке соединения ионов кальция. Проведен совместный количественный анализ экспериментальных температурных зависимостей кинетических коэффициентов, что позволило определить значения основных параметров энергетического спектра и системы носителей заряда в исследованных образцах. Проанализированы причины изменений характера влияния примесей лантана и празеодима, вызванных наличием ионов кальция в решетке, и показано, что они различаются. Полученные данные о модификации структуры энергетического спектра под действием легирования позволили объяснить особенности концентрационных зависимостей критической температуры в исследованных системах.

**Ключевые слова:** высокотемпературный сверхпроводник, легирование, критическая температура, термоэдс, коэффициент Нернста – Эттингсгаузена, энергетический спектр

**Ссылка при цитировании:** Гасумянц В. Э. Сравнительное исследование и анализ коэффициентов термоэдс и Нернста – Эттингсгаузена в системах  $Y_{0,85}Ca_{0,15}Ba_{2-x}La_xCu_3O_y$  и  $Y_{0,85-x}Ca_{0,15}Pr_xBa_2Cu_3O_y$  // Научно-технические ведомости СПбГПУ. Физико-математические науки. 2021. Т. 14. № 4. С. 21–39. DOI: 10.18721/JPM.14402

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## Introduction

Ever since high-temperature superconductors (HTSC) were first discovered 35 years ago, numerous studies have analyzed various characteristics of this class of materials. However, many unusual properties of such compounds yet remain to be interpreted correctly. This concerns not only the mechanism of high-temperature superconductivity but also some other properties of HTSC materials, including those observed in the normal state. The primary reason for this is that the structure of the energy spectrum in these compounds and the main parameters characterizing the charge carrier system in the normal state remain largely unknown. As a result, the standard approaches to analyzing the properties of classical objects of condensed matter physics turn out to be inapplicable to HTSC compounds in most cases, so many of their properties are often explained on the basis of various phenomenological models.

Quantitative analysis of electron transport is a well-known method for obtaining information on the parameters of the charge carrier system in the normal state. The specifics of electron transport observed in HTSC materials indicate that the standard theory of transport phenomena cannot be used for this purpose [1–5]. Consequently, various models, frequently using fundamentally different approaches, have been proposed to interpret the temperature dependences of transport coefficients in HTSC materials. One of these models is the narrow-band model that we have developed [4, 6]. It allows to qualitatively describe the nature of temperature dependences for all four main transport coefficients (resistivity  $\rho$ , thermopower  $S$ , Hall coefficient  $R_H$ , Nernst coefficient  $Q$ ) in HTSC materials of various systems; combined quantitative analysis of the temperature dependences  $S(T)$  and  $Q(T)$  in turn allows finding the main parameter values for the energy spectrum and the charge carrier system in the normal state. We have firmly established in our previous studies that the narrow-band model can be effectively applied to analyzing the modification of the energy spectrum in the  $\text{YBa}_2\text{Cu}_3\text{O}_y$  HTSC system under doping by different impurities (see, for example, [4, 5, 7] and references therein). The model can therefore be used to identify the nature and mechanism of influence of the given substitutions on the parameters of the electron system in the normal state. Notably, while different approaches have been proposed for describing the thermopower and the Hall coefficient (see, for example, [8–16]), the behavior of the Nernst coefficient is analyzed in the literature either in a mixed state (below the critical temperature  $T_c$ ), or in a rather narrow temperature range above this temperature. A strong increase in the absolute values of the Nernst coefficient was discovered in the latter case for a number of doped HTSC systems [17–21]. To explain this behavior, the idea of the possibility of boson formation in the normal state region was proposed [18, 22–24].

Thus, there are no alternatives to the narrow-band model for describing the dependences  $Q(T)$  in a wide temperature range in the normal state.

It is well known that superconductivity is preserved in the  $\text{YBa}_2\text{Cu}_3\text{O}_y$  system upon partial substitution of all metal components in the lattice [25]. Moreover, many cation substitutions have a similar effect both on the value of  $T_c$  and on the behavior of transport coefficients in the normal phase. An increase in the impurity content leads to a drop in the critical temperature and a simultaneous increase in the absolute values of all transport coefficients, accompanied by a qualitatively similar transformation of their temperature dependences [4]. However, calcium, which replaces yttrium in the  $\text{YBa}_2\text{Cu}_3\text{O}_y$  lattice, holds a special place among possible cation substitutions. The nature of the influence that calcium has on the critical temperature fundamentally depends on the general composition of  $\text{YBa}_2\text{Cu}_3\text{O}_y$  samples. Increasing the calcium content in samples close to stoichiometric composition suppresses the superconducting properties, the same as in the case of other impurities [7, 26–28]. However, if an oxygen deficiency or another impurity is first introduced into the  $\text{YBa}_2\text{Cu}_3\text{O}_y$  system so that  $T_c$  is reduced, additional doping by calcium restores superconductivity [7, 28–35]. In this case, the variation in the absolute values of the transport coefficients does not correlate with the variation in the value of  $T_c$ , and their temperature dependences acquire a number of additional characteristics [7, 36–40]. We have earlier concluded from analyzing the temperature dependences of the thermopower in calcium-containing samples with different compositions that the reason for these specific features is that calcium directly affects the structure of the energy spectrum in  $\text{YBa}_2\text{Cu}_3\text{O}_y$ , forming an additional peak in the density-of-states (DOS) function located in the immediate vicinity of the Fermi level [7, 28].

Obviously, the presence of this peak should alter the nature of the influence from other cation substitutions on different properties of the  $\text{YBa}_2\text{Cu}_3\text{O}_y$  system if calcium ions are preliminarily introduced into it in a fixed content.

Based on the above, our goal consisted in comparative study and quantitative analysis of the thermopower and Nernst coefficients in  $\text{Y}_{0.85}\text{Ca}_{0.15}\text{Ba}_{2-x}\text{La}_x\text{Cu}_3\text{O}_y$  and  $\text{Y}_{0.85-x}\text{Ca}_{0.15}\text{Pr}_x\text{Ba}_2\text{Cu}_3\text{O}_y$  systems. The mechanisms of influence of lanthanum and praseodymium impurities on the properties of  $\text{YBa}_2\text{Cu}_3\text{O}_y$  in cases of single substitutions are very different. The effect of lanthanum is mainly associated with modifying the state of the oxygen subsystem resulting from the La introduction into the lattice, in particular, with the oxygen content increased to over-stoichiometric values ( $y > 7.0$ ) [41–44]. Praseodymium doping does not produce a significant change in the oxygen content in the samples, however, this impurity directly affects the structure of the energy spectrum in  $\text{YBa}_2\text{Cu}_3\text{O}_y$  due to hybridization of praseodymium ion states with conduction band states [45–48]. Additional calcium ions in the lattice can considerably affect how these mechanisms evolve.

### Experimental samples and measurement procedure

The studies involved ceramic samples with the  $\text{Y}_{0.85-x}\text{Ca}_{0.15}\text{Pr}_x\text{Ba}_2\text{Cu}_3\text{O}_y$  and  $\text{Y}_{0.85-x}\text{Ca}_{0.15}\text{Pr}_x\text{Ba}_2\text{Cu}_3\text{O}_y$  ( $x = 0-0.3$ ) compositions, prepared by standard solid-phase synthesis from high-purity oxides and carbonates. The samples were synthesized in air by three-stage annealing with the temperature gradually increased from 900 to 930 °C and intermediate regrinding. Samples of the  $\text{Y}_{0.85}\text{Ca}_{0.15}\text{Ba}_{2-x}\text{La}_x\text{Cu}_3\text{O}_y$  system were additionally annealed in flowing oxygen at  $T = 450$  °C for 10 hours; this annealing was not performed for  $\text{Y}_{0.85-x}\text{Ca}_{0.15}\text{Pr}_x\text{Ba}_2\text{Cu}_3\text{O}_y$  samples.

The temperature dependences were obtained for all samples for the resistivity, as well as for the thermopower and Nernst coefficient in the temperature range  $T = T_c - 300$  K for  $\rho(T)$  and  $S(T)$  dependences, or  $T = 80-320$  K for  $Q(T)$  dependences. Resistivity was measured by the four-probe ac method with frequency and phase selection. The thermopower was measured relative to copper electrodes with a temperature gradient of about 2 K across the sample. The Nernst coefficient was measured in a constant magnetic field  $B = 1.8$  T using thin (about 1 mm thick) samples, allowing to reach high temperature gradients (up to  $\nabla T = 100$  K/cm). The voltages were measured in two opposite directions of the magnetic field to eliminate the spurious components in the signal that are even functions of the magnetic field.

### Experimental results and discussion

The  $\rho(T)$  dependences used to determine the critical temperatures exhibited a linear decrease in resistivity with decreasing temperature, which is typical for doped yttrium HTSC at relatively low doping levels [1, 3, 4]. The variation in  $T_c$  with an increase in the doping level for both series of samples is shown in Fig. 1. Let us note that the critical temperature for the initial samples in the two series, as well as the values of the transport coefficients and calculated parameters given below, are somewhat different because different techniques were used for synthesis (the  $\text{Y}_{0.85}\text{Ca}_{0.15}\text{Ba}_{2-x}\text{La}_x\text{Cu}_3\text{O}_y$  samples were additionally saturated with oxygen). Nevertheless, the trends in the variation of all these parameters under doping still can be compared, which was the purpose of our study. Apparently, increasing the praseodymium and lanthanum contents leads to a qualitatively similar change in the critical temperature:  $T_c$  remains almost unchanged in the range  $x \leq 0.175-0.200$ , dropping rather sharply with a further increase in the doping level. We should note that the  $T_c(x)$  dependences are qualitatively different for similar single substitutions (in the absence of calcium ions in the lattice).  $T_c$  increases slightly in the range  $x = 0-0.1$  for the  $\text{YBa}_{2-x}\text{La}_x\text{Cu}_3\text{O}_y$  system with an oxygen content close to stoichiometric, gradually decreasing afterwards; on the other hand, the critical temperature in the  $\text{Y}_{1-x}\text{Pr}_x\text{Ba}_2\text{Cu}_3\text{O}_y$  system decreases gradually over the entire range of praseodymium content. Thus, the obvious reason why the  $T_c(x)$  dependences start behaving differently in  $\text{Y}_{0.85-x}\text{Ca}_{0.15}\text{Pr}_x\text{Ba}_2\text{Cu}_3\text{O}_y$  and  $\text{Y}_{0.85}\text{Ca}_{0.15}\text{Ba}_{2-x}\text{La}_x\text{Cu}_3\text{O}_y$  samples, compared to cases of corresponding single substitutions, is the presence of Ca ions in these samples. This is due to the effect of Fermi-level pinning in the energy range near the local peak in the DOS function [7, 35], which, according to our previous data, is formed due to introducing calcium ions into the lattice.

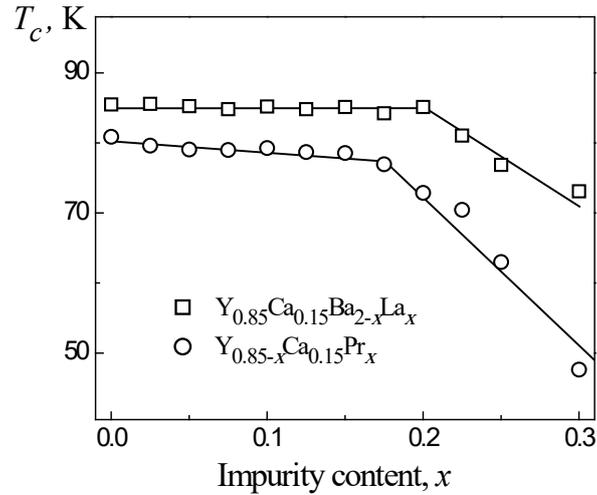


Fig. 1. Critical temperature as a function of doping level in  $Y_{0.85-x}Ca_{0.15}Pr_xBa_2Cu_3O_y$  and  $Y_{0.85}Ca_{0.15}Ba_{2-x}La_xCu_3O_y$  samples

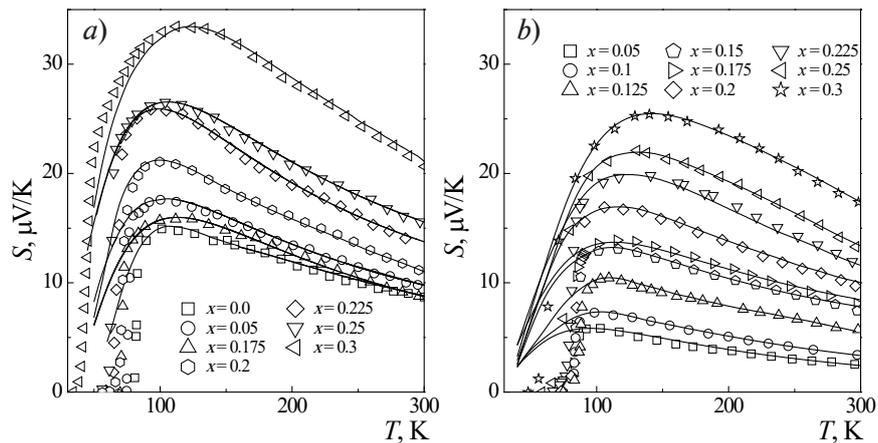


Fig. 2. Experimental (symbols) and calculated (lines) temperature dependences of the thermopower in  $Y_{0.85-x}Ca_{0.15}Pr_xBa_2Cu_3O_y$  (a) and  $Y_{0.85}Ca_{0.15}Ba_{2-x}La_xCu_3O_y$  (b) samples; the calculations were carried out within the narrow-band model

The experimental temperature dependences of the thermopower and the Nernst coefficient obtained for the two systems are shown in Figs. 2 and 3. The same as in all doped samples of the  $YBa_2Cu_3O_y$  family, the  $S(T)$  curves have a pronounced peak whose position on the temperature scale depends on the doping level. However, another characteristic of the  $S(T)$  dependences typical for yttrium HTSC, namely that the thermopower varies very weakly at high temperatures [2, 4] (particularly pronounced for the coefficient's small absolute values), is not observed in the given samples. An almost linear decrease in  $S$  is observed instead with the temperature increasing up to  $T = 300$  K. This behavior of the coefficient is explained by the influence of calcium impurity. An increase in Ca content is known to lead to a gradual increase in the slope of the  $S(T)$  curves in the high-temperature region [7]. This feature is observed in calcium-containing samples of the  $YBa_2Cu_3O_y$  system regardless of the way of their additional doping techniques, which is associated with the influence of calcium on the structure of the band responsible for the conduction process in this compound in the normal state [7, 28, 31–40]. Thus, the  $S(T)$  dependences for the given systems exhibit all of the characteristics typical for the behavior of the Thermopower in doped HTSC samples of the yttrium family whose lattice contains calcium ions.

The  $Q(T)$  dependences are in general qualitatively similar to those observed for other doped samples of the yttrium family [5], however, certain additional features are observed, as in the case of the thermopower. A pronounced peak is preserved on the  $Q(T)$  dependence in the high-temperature region with an increase in the doping level for most single substitutions; the specific position of this peak depends on the type and level of doping [2]. This peak does not appear for the systems considered: the Nernst coefficient in  $Y_{0.85-x}Ca_{0.15}Pr_xBa_2Cu_3O_y$  remains almost unchanged for all samples at  $T > 250$  K (see Fig. 3,*a*), while the  $Q(T)$  dependence in  $Y_{0.85}Ca_{0.15}Ba_{2-x}La_xCu_3O_y$  with a high lanthanum content becomes decreasing with decreasing temperature over the entire range  $T < 320$  K (see Fig. 3,*b*). Another characteristic of the  $Q(T)$  dependences, only observed for slightly doped samples in the case of single substitutions, is the transition to negative  $Q$  values in the low-temperature region; this characteristic is observed for all samples, including those with the maximum doping level. Thus, the  $Q(T)$  dependences for the considered systems gain additional characteristics due to the presence of calcium ions in the lattice, compared to the cases of single La→Ba and Pr→Y substitutions.

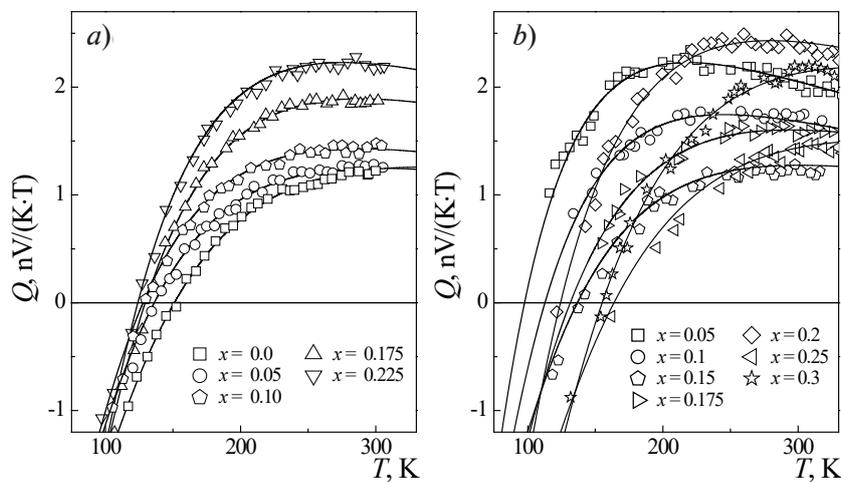


Fig. 3. Experimental (symbols) and calculated (lines) temperature dependences of the Nernst coefficient in  $Y_{0.85-x}Ca_{0.15}Pr_xBa_2Cu_3O_y$  (*a*) and  $Y_{0.85}Ca_{0.15}Ba_{2-x}La_xCu_3O_y$  (*b*) samples; the calculations were carried out within the narrow-band model

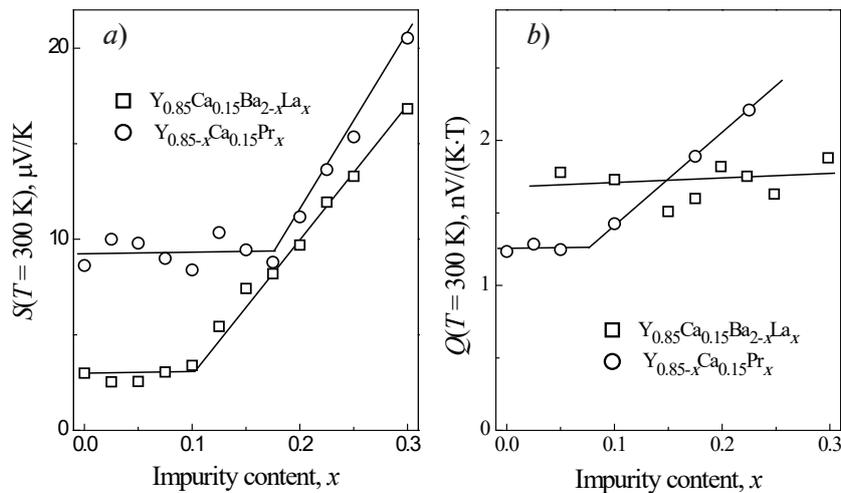


Fig. 4. Values of thermopower (*a*) and Nernst coefficient (*b*) as functions of doping level in  $Y_{0.85-x}Ca_{0.15}Pr_xBa_2Cu_3O_y$  and  $Y_{0.85}Ca_{0.15}Ba_{2-x}La_xCu_3O_y$  samples;  $T = 300$  K

The specific effect that the presence of calcium ions in the  $\text{YBa}_2\text{Cu}_3\text{O}_y$  lattice has on the nature of the transformations undergone by the electron properties of this compound due to the La→Ba and Pr→Y substitutions is best exhibited in the variations of the absolute values of the thermopower and the Nernst coefficient with increasing doping level. Single substitutions of the type considered are known to result in a gradual increase in the values of these coefficients, including at room temperature ( $S_{300}$  and  $Q_{300}$ , respectively) [5, 43, 44, 48]. The  $S_{300}(x)$  and  $Q_{300}(x)$  dependences have a different form in  $\text{Y}_{0.85-x}\text{Ca}_{0.15}^x\text{Pr}_x\text{Ba}_2\text{Cu}_3\text{O}_y$  and  $\text{Y}_{0.85}\text{Ca}_{0.15}\text{Ba}_{2-x}\text{La}_x\text{Cu}_3\text{O}_y$  systems (Fig. 4).

The value of the thermopower remains unchanged at low impurity contents (up to  $x = 0.175$  and  $x = 0.100$  for the La→Ba and Pr→Y substitutions, respectively), subsequently increasing almost linearly (see Fig. 4,*a*). Thus, the  $S_{300}$  values characterizing the properties of the electron system in the normal state, and the critical temperature of the superconducting transition  $T_c$  vary in a similar manner in the systems considered (compare Fig. 1 and Fig. 4,*a*), although the transition from constant to increasing  $S_{300}$  values occurs at lower impurity concentrations than the transition to decreasing  $T_c$  values. The reason for this is that both of these quantities are directly related to the position of the Fermi level, and the type of  $S_{300}(x)$  dependences serves to additionally prove that Fermi-level pinning occurs in the given systems inside the peak of calcium states.

It is evident from Fig. 4,*b* that the  $Q_{300}(x)$  dependences look different in the systems considered, in contrast to the Thermopower. The same as  $S_{300}$ , the  $Q_{300}$  values in the  $\text{Y}_{0.85-x}\text{Ca}_{0.15}^x\text{Pr}_x\text{Ba}_2\text{Cu}_3\text{O}_y$  samples do not vary in the slightly doped range (but only up to  $x = 0.05$ , i.e., at noticeably lower values than in the case of the thermopower), and subsequently increase. Conversely, the  $Q_{300}$  value varies weakly over the entire range of lanthanum contents in the  $\text{Y}_{0.85}\text{Ca}_{0.15}\text{Ba}_{2-x}\text{La}_x\text{Cu}_3\text{O}_y$  system. Therefore, the variations observed in the values of  $S_{300}$  and  $Q_{300}$  with increasing doping levels are uncorrelated with each other, especially in the case of  $\text{Y}_{0.85}\text{Ca}_{0.15}\text{Ba}_{2-x}\text{La}_x\text{Cu}_3\text{O}_y$ , while such a correlation is always observed for single substitutions in the  $\text{YBa}_2\text{Cu}_3\text{O}_y$  system [5]. This characteristic of the systems means that the variations exhibited by the values of the thermopower and the Nernst coefficient under doping depends on the effect of impurities on various structural parameters of the energy spectrum in the given compounds.

Thus, the experimental data obtained indicate that the effect that doping  $\text{YBa}_2\text{Cu}_3\text{O}_y$  with lanthanum and praseodymium has on the critical temperature and the behavior of the thermopower and the Nernst coefficient takes on a different character in the presence of calcium ions in the lattice of this compound. Next, let us carry out quantitative analysis of the experimental results within the narrow-band model to uncover the mechanisms behind the above changes, as well as the reasons for the differences detected in the influence of the two substitutions considered on the behavior of the Nernst coefficient.

### Analysis of the obtained experimental data

The results were interpreted using the approach we developed based on combined quantitative analysis of the temperature dependences of the thermopower and the Nernst coefficient within the phenomenological model assuming that the energy spectrum of HTSC materials contains either a narrow conduction band or a narrow peak of the DOS function  $D(E)$  (referred to as the narrow-band model from now on) [5, 49]. The condition of the band narrowness (consisting in its half-width being comparable with the magnitude of the Fermi smearing) allows approximating the DOS function, the differential conductivity  $\sigma(E)$  and the Hall conductivity  $\sigma_H(E)$  by rectangles (generally, with different widths) [4–6, 49]. Additionally accounting for the possible asymmetry of the DOS functions and the dispersion law results in shifting the center of the rectangle approximating the function  $\sigma(E)$ , as well as the point where the function  $\sigma_H(E)$  reverses sign relative to the center of the rectangle approximating the function  $D(E)$  [5, 49]. Using standard expressions for kinetic integrals within such approximations, we managed to obtain the analytical expressions describing the temperature dependences of the electrochemical potential and all main transport coefficients [4–6, 49]. The expressions for the resistivity and the Hall coefficient include the unknowns of the band-averaged values of the functions  $\sigma(E)$  and/or  $\sigma_H(E)$ , which only allows comparing the experimental and calculated temperature dependences of these coefficients qualitatively.

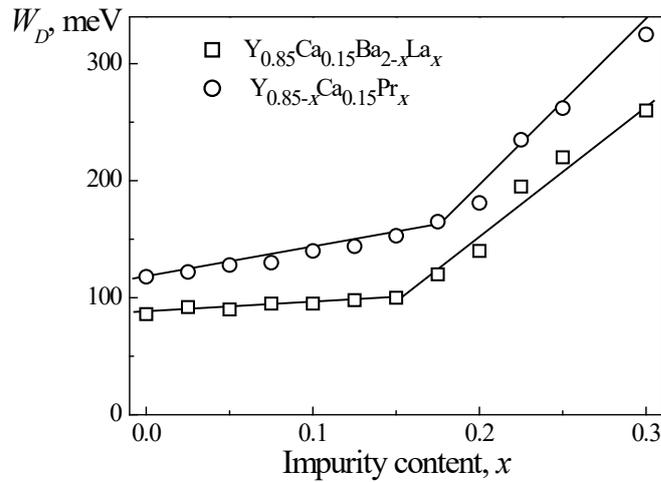


Fig. 5. Total effective width of the conduction band as a function of doping level in  $Y_{0.85-x}Ca_{0.15}Pr_xBa_2Cu_3O_y$  and  $Y_{0.85}Ca_{0.15}Ba_{2-x}La_xCu_3O_y$  samples

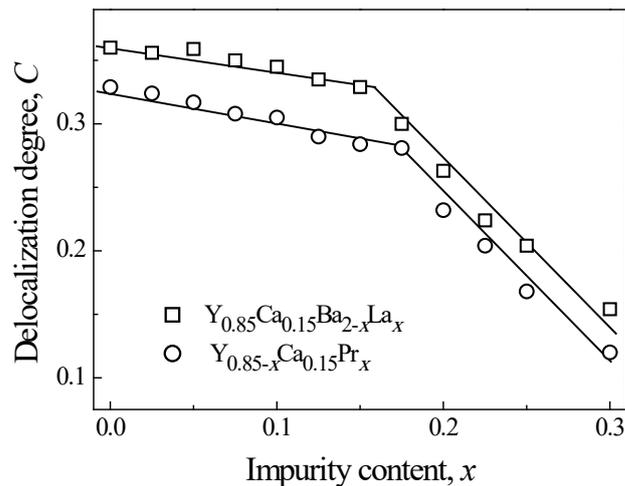


Fig. 6. Degree of state delocalization as a function of doping level in  $Y_{0.85-x}Ca_{0.15}Pr_xBa_2Cu_3O_y$  and  $Y_{0.85}Ca_{0.15}Ba_{2-x}La_xCu_3O_y$  samples

Due to the form of the corresponding kinetic integrals for the thermopower and the Nernst coefficient are reduced, so that the expressions obtained for calculating  $S(T)$  and  $Q(T)$  can be applied to quantitative analysis of the experimental data. The procedure for deriving all these expressions and their specific form are given in [4–6, 49].

In the most general case, the calculated expressions for the thermopower and the Nernst coefficient contain six model parameters, each of them with a clear physical meaning. These parameters are  $W_D$  and  $W_\sigma$ , the total effective width of the conduction band and the effective width of the energy interval occupied by conducting (delocalized) states (corresponding to the widths of the rectangles approximating the functions  $D(E)$  and  $\sigma(E)$ );  $F$ , the degree of the band filling with electrons, defined as the ratio of the total number of electrons to the total number of states in the band;  $b$ , the degree of band asymmetry (determining the absolute value of the energy shift  $bW_D$  between the centers of the rectangles  $D(E)$  and  $\sigma(E)$ );  $k$ , the asymmetry degree of the dispersion law (determining the absolute value of the energy shift  $kW_D$  between the center of the rectangle  $D(E)$  and the point at which  $\sigma_H(E)$  reverses sign;  $u$ , the value of the band-averaged electron mobility. Despite the relatively large number of



fitting parameters, their values can be defined almost unambiguously by combined analysis of the experimental data obtained for the  $S(T)$  and  $Q(T)$  dependences, measured in the same samples. For this purpose, the experimental data for the thermopower whose calculated temperature dependence is determined by four of the model parameters ( $W_D$ ,  $W_\sigma$ ,  $F$  and  $b$ ) should be analyzed at the first stage. Next, the values found are substituted into the expressions for calculating the Nernst coefficient to determine the values of the last two parameters ( $k$  and  $u$ ), slightly refining the values of the first four parameters if necessary [5, 49].

The described method was used to analyze the experimental data obtained for the  $S(T)$  and  $Q(T)$  dependences for the samples of the  $Y_{0.85-x}Ca_{0.15}Pr_xBa_2Cu_3O_y$  and  $Y_{0.85}Ca_{0.15}Ba_{2-x}La_xCu_3O_y$  system presented above. Figs. 2 and 3 show the calculated curves obtained through this analysis, proving that we managed to achieve good agreement with the experimental data in all cases. Thus, we found the parameter values for the energy spectrum and the system of charge carriers for samples of all compositions considered. Comparative analysis of the dependences of these parameters on the dopant content is given below.

Let us first consider the results obtained from analysis of the  $S(T)$  dependences. The band asymmetry parameter is practically unchanged for all samples considered, equaling  $b \approx -0.018$ . This agrees with the earlier conclusion that introducing calcium into the  $YBa_2Cu_3O_y$  lattice leads to an asymmetry of the conduction band in all cases; the parameter describing this asymmetry changes by the law  $b \approx -0.12z$ , where  $z$  is the calcium content (remaining unchanged in our samples) [7, 35]. The variations in the energy parameters of the conduction band are shown in Figs. 5 and 6. Instead of the parameter  $W_\sigma$ , we use the ratio  $C = W_\sigma/W_D$ , characterizing the degree of band state delocalization [4, 6]. The total effective band width  $W_D$  varies insignificantly in the slightly doped range (up to  $x = 0.150$  and  $x = 0.175$  for praseodymium and lanthanum impurities, respectively), especially in the case of La→Ba substitution; further increasing the doping level substantially broadens the conduction band. The degree of state delocalization qualitatively varies in a similar manner: the fraction of localized states at the edges of the band increases rather weakly with increasing  $x$  in the slightly doped range (a slight decrease in the value of the parameter  $C$  is observed) and increases strongly at  $x > 0.150$  or  $x > 0.175$ .

Thus, doping modifies the conduction band in both systems in a similar manner, moreover, the variation in the band's total effective width correlates with the variation in the critical temperature (compare Fig. 1 and Fig. 5), which is a distinct characteristic of doped yttrium HTSC for many types of substitutions [4]. However, the physical mechanisms behind this modification are fundamentally different in the two systems. The  $W_D$  and  $C$  values remain almost unchanged under single doping with lanthanum in the  $YBa_{2-x}La_xCu_3O_y$  system (in the absence of additional calcium ions in the lattice) at  $x < 0.15-0.10$  for samples close to oxygen stoichiometry; an increase in the former and a decrease in the latter are observed with a further increase in  $x$  [48, 43]. According to [43], the reason for this is that lanthanum has a higher valence in the  $YBa_{2-x}La_xCu_3O_y$  lattice than the barium it substitutes, so increasing its content leads to an increase in the value of the oxygen content  $y$ . If the lanthanum content is low, the oxygen positions in the CuO chains, remaining vacant in the undoped sample, are filled, leading to a partial ordering of the oxygen sublattice of the compound, which compensates for the disorder introduced by lanthanum ions. According to the Anderson localization model, this is what produces the slight variations in the effective width of the conduction band and the degree of state localization. A further increase in  $x$  in the  $YBa_{2-x}La_xCu_3O_y$  compound is accompanied by filling of apical oxygen positions, which, along with a significant increase in lanthanum content, results in increasing the degree of lattice disorder and, accordingly, increasing the value of  $W_D$ . Introducing additional calcium into the lattice tends to decrease the oxygen content [26–29]. Consequently, the chain oxygen positions in  $Y_{0.85}Ca_{0.15}Ba_{2-x}La_xCu_3O_y$  are filled up to the stoichiometric value  $y = 7$  in a wider range of lanthanum contents. This is why the range where  $W_D$  and  $C$  values vary weakly is extended compared with the  $YBa_{2-x}La_xCu_3O_y$  system. In this case, these values vary weakly rather than remain unchanged (as in  $YBa_{2-x}La_xCu_3O_y$ ) because the disorder degree in the lattice is generally increased due to high lanthanum contents and additional calcium ions introduced. Thus, lanthanum in  $Y_{0.85}Ca_{0.15}Ba_{2-x}La_xCu_3O_y$  indirectly affects the energy parameters of the band by changing the oxygen content, while the mechanism for modifying the conduction band remains unchanged.

A different situation is observed for  $Y_{0.85}Ca_{0.15}Ba_2Cu_3O_y$  doped with praseodymium. This impurity is close to isovalent and has virtually no effect on the oxygen content in the samples [45, 48]. Nevertheless, a gradual and substantial increase in the  $W_D$  values (up to  $W_D = 260$  meV at  $x = 0.2$ ) is observed in the  $Y_{1-x}Pr_xBa_2Cu_3O_y$  system with an increase in  $x$ , accompanied by a strong increase in the degree of state localization (decrease in the parameter  $C$ ) due to hybridization between band states and praseodymium ion states, which directly affects the energy structure of the conduction band [4, 48]. The data for the  $Y_{0.85-x}Ca_{0.15}Pr_xBa_2Cu_3O_y$  system can be interpreted based on our earlier findings, establishing that the calcium and praseodymium ions simultaneously introduced into the lattice interact with each other, weakening the above effect [40]. It can be seen from Fig. 5 that the  $W_D(x)$  and  $C(x)$  dependences change their nature at  $x = 0.175$ , i.e., at the praseodymium content close to the calcium content introduced into the  $Y_{0.85-x}Ca_{0.15}Pr_xBa_2Cu_3O_y$  system. We can thus conclude that weakening the praseodymium effect on the structure of the conduction band, observed at  $x = 0-0.175$ , is related to the calcium ions compensating for praseodymium influence. If praseodymium content becomes higher, its ions affect the structure of the conduction band in a manner similar to the

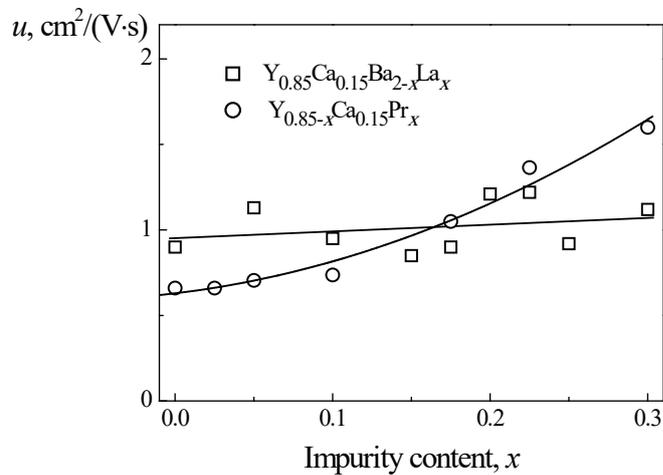


Fig. 7. Electron mobility as a function of doping level in  $Y_{0.85-x}Ca_{0.15}Pr_xBa_2Cu_3O_y$  and  $Y_{0.85}Ca_{0.15}Ba_{2-x}La_xCu_3O_y$  samples

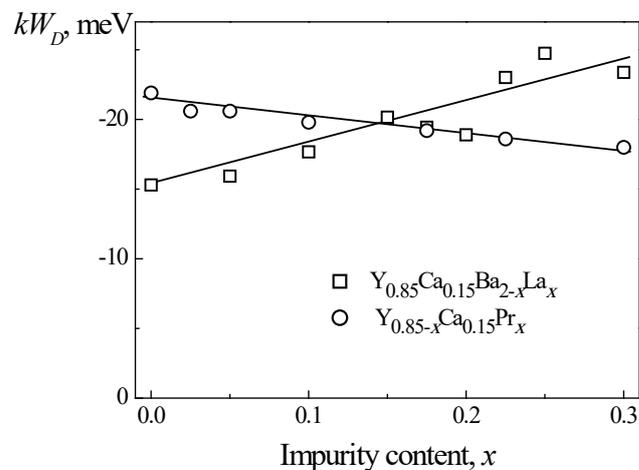


Fig. 8. Asymmetry of dispersion law as a function of doping level in  $Y_{0.85-x}Ca_{0.15}Pr_xBa_2Cu_3O_y$  and  $Y_{0.85}Ca_{0.15}Ba_{2-x}La_xCu_3O_y$  samples

case of single doping with this impurity, which is what enhances the  $W_D(x)$  and  $C(x)$  dependences at  $x > 0.175$ . Thus, unlike the lanthanum impurity in the  $Y_{0.85}Ca_{0.15}Ba_{2-x}La_xCu_3O_y$  system, praseodymium in the  $Y_{0.85-x}Ca_{0.15}Pr_xBa_2Cu_3O_y$  system directly affects the structure of the conduction band, but the mechanism behind this effect changes after the praseodymium content corresponding to the number of calcium ions introduced into the lattice is reached.

We should note that the  $F(x)$  dependence for the  $Y_{0.85-x}Ca_{0.15}Pr_xBa_2Cu_3O_y$  system also behaves differently than in the case of single doping with praseodymium: the band filling degree decreases in the slightly doped range and increases in the heavily doped one. This goes on to confirm the conclusion that the mechanism by which praseodymium affects the parameters of the normal state in the  $Y_{0.85-x}Ca_{0.15}Pr_xBa_2Cu_3O_y$  system is altered at  $x \approx 0.175$ .

Let us now consider the results obtained from analysis of the experimental data for the temperature dependences of the Nernst coefficient. Fig. 7 shows the dependences of electron mobility on the content of the impurities introduced. Fig. 8 shows similar dependences for the energy shifts of the point, where the function  $\sigma_H(E)$  reverses sign, from the center of the conduction band  $kW_D$ , determined from the values  $\sigma_H$  found for the degree of the dispersion law asymmetry. It is necessary to note that the mobility found from analyzing the  $Q(T)$  dependences within the narrow-band model is not the ‘Nernst’ mobility often used in semiconductor physics and defined simply as  $Q/(k_B/e)$ , where  $k_B$  is the Boltzmann constant,  $e$  is the electron charge. It is in this case the true mobility of charge carriers ( $u = e\tau/m$ , where  $\tau$  is the relaxation time, and  $m$  is the effective electron mass), averaged over the entire narrow conduction band. The following circumstances should be taken into account when analyzing the variations in the mobility with increasing doping level. As discussed above, the degree of lattice disorder (which can be estimated from the  $C(x)$  dependence) changes with increasing impurity contents; the effective width of the conduction band  $W_D$  changes as well. Both of these factors directly affect the value of the electron mobility. Increasing the degree of disorder increases the scattering frequency, i.e., decreases the relaxation time and, accordingly, the mobility. On the other hand, as the band broadens, the effective electron mass decreases, leading to an increase in the mobility. A typical scenario for HTSC is that a broadening of the band and an increase in the degree of state localization due to the Anderson mechanism [4] occur simultaneously under doping. These two factors have opposing effects on the value of  $u$ , so that the one prevailing decides the resulting form of the  $u(x)$  dependence.

It can be seen from Fig. 7 that the mobility value remains almost unchanged ( $u \approx 1 \text{ cm}^2/(\text{V}\cdot\text{s})$ ) in the  $Y_{0.85}Ca_{0.15}Ba_{2-x}La_xCu_3O_y$  system, but increases with increasing  $x$ , albeit rather weakly, in the  $Y_{0.85}Ca_{0.15}Ba_{2-x}La_xCu_3O_y$  system. Fairly weak broadening of the band and insignificant increase in the fraction of localized states are observed in the first system in the range  $x \leq 0.15$  (see Figs. 5 and 6). As a result, the mobility value remains almost unchanged given a simultaneous decrease in  $\tau$  and  $m$ . At  $x > 0.15$ , the band broadens more strongly, but the degree of state localization shows the same trend, thus ultimately preserving a constant value of the mobility. Even though the  $W_D(x)$  and  $C(x)$  dependences in the  $Y_{0.85-x}Ca_{0.15}Pr_xBa_2Cu_3O_y$  system start behaving differently at  $x \approx 0.175$ , the band broadens more substantially over the entire doping range compared to the  $Y_{0.85}Ca_{0.15}Ba_{2-x}La_xCu_3O_y$  system. As a result, the effect from the decrease in the effective electron mass is not fully compensated by the decreased relaxation time, and the mobility value weakly increases.

As for the asymmetry of the dispersion law, it can be seen from Fig. 8 that the change in the energy shift of the point where the  $\sigma_H(E)$  function reverses sign displays an opposite behavior with an increase in the doping level in the two systems considered. Note that in contrast to the asymmetry of the DOS function (determined in the model used by the value of the parameter  $b$  and observed for the yttrium HTSC only under doping with calcium [4]), the asymmetry of the dispersion law is characteristic for samples of any composition and is a common property of this law for  $YBa_2Cu_3O_y$  [5]. Increasing the praseodymium content in the  $Y_{0.85-x}Ca_{0.15}Pr_xBa_2Cu_3O_y$  system leads to a decrease in the absolute value of  $kW_D$ , which gives further evidence that this impurity directly affects the structure of the energy spectrum. As for the  $Y_{0.85}Ca_{0.15}Ba_{2-x}La_xCu_3O_y$  system, the absolute value of  $kW_D$  increases, albeit slightly (by less than 8 meV in the entire doping range considered). Lanthanum is believed to have an indirect effect on the properties of  $YBa_2Cu_3O_y$  (primarily through altering the state of the oxygen subsystem). Our results show that this impurity nevertheless does directly contribute towards modifying the structure of the conduction band.

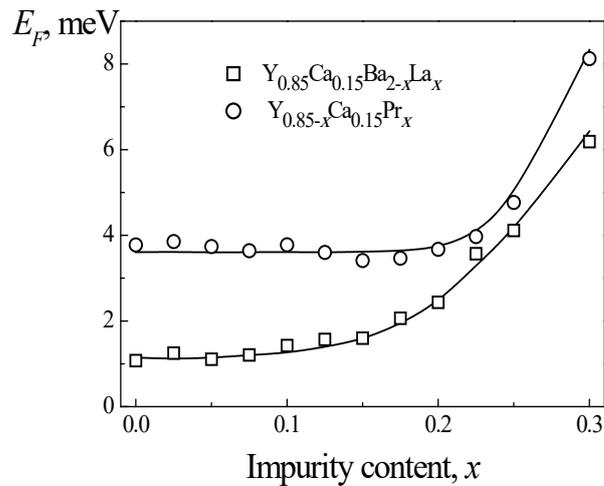


Fig. 9. Position of the Fermi level as a function of doping level in  $Y_{0.85-x}Ca_{0.15}Pr_xBa_2Cu_3O_y$  and  $Y_{0.85}Ca_{0.15}Ba_{2-x}La_xCu_3O_y$  samples

In conclusion, let us compare the doping-induced changes in the energy spectrum of the systems considered in the normal state with the ones superconducting properties. According to the results obtained earlier for doped HTSC of the  $YBa_2Cu_3O_y$  system, the value of the critical temperature turns out to be directly related to the value of the DOS function at the Fermi level  $D(E_F)$ , as described by the classical theory of superconductivity [4]. In turn,  $D(E_F)$  depends on the effective band width within the method that we use for approximating the function  $D(E)$ : the larger the  $W_D$  value, the smaller (provided that the total number of electronic states in the band is preserved) the  $D(E_F)$  value. Since the conduction band broadens rather dramatically for the majority of non-isovalent cation substitutions in  $YBa_2Cu_3O_y$  with an increase in the doping level, other characteristics of the energy spectrum structure have a much smaller effect on the  $D(E_F)$  value; as a result, there is a correlation close to universal between the  $T_c$  and  $W_D$  values for the  $YBa_2Cu_3O_y$  system with various types of substitutions [4]. However, if the lattice of this compound contains calcium ions, the peculiar effect of this impurity on the structure of the conduction band should be taken into account, namely, the appearance of an additional peak of calcium-induced states near the middle of the band. In this case, the positions of the Fermi level in samples of various compositions should be detected to reveal the trends in the variation of  $D(E_F)$ . The position of  $E_F$  relative to the center of the energy interval corresponding to the conduction states in the region of low (i.e., close to  $T_c$ ) temperatures can be calculated for an asymmetric band by the formula  $E_F = (F - 0.5)W_D - bW_D$  [50].

The results of this calculation for the systems considered are shown in Fig. 9. It can be seen that the  $E_F$  value in the slightly doped range either varies very slightly (for  $Y_{0.85}Ca_{0.15}Ba_{2-x}La_xCu_3O_y$ ), or in fact remains constant (for  $Y_{0.85-x}Ca_{0.15}Pr_xBa_2Cu_3O_y$ ), while the Fermi level begins to shift up the energy scale with a sufficiently strong increase in the doping level. This suggests that Fermi-level pinning occurs at low impurity concentrations inside the peak of calcium states, which is what contributes, along with a weak broadening of the conduction band, to preserving or slightly reducing the  $D(E_F)$  and, respectively,  $T_c$  values (see Fig. 1). If the impurity content rises above  $x = 0.15 - 0.20$ , the position of the Fermi level leaves the region of this peak, while the conduction band broadens dramatically, resulting in a substantial decrease in the  $D(E_F)$  and  $T_c$  values.

Thus, the results obtained from quantitative analysis of the  $S(T)$  and  $Q(T)$  dependences allow not only to establish the mechanisms by which the given impurities influence the structure of the energy spectrum and the parameters of the charge carrier system in the studied systems, but also to explain the trends observed in the variation of the critical temperature with an increase in the content of these impurities.

### Conclusion

This paper presents a comparative experimental study on the behavior of the thermopower and the Nernst coefficient in doped yttrium HTSC with the  $Y_{0.85}Ca_{0.15}Ba_{2-x}La_xCu_3O_y$  and  $Y_{0.85-x}Ca_{0.15}Pr_xBa_2Cu_3O_y$  compositions as well as quantitative analysis of the temperature dependences of these coefficients based on the narrow-band model. We have obtained the following findings and drawn the following conclusions.

1. The dependences of the critical temperature and absolute values of the thermopower and the Nernst coefficient on the content of lanthanum impurities at barium positions, as well as praseodymium impurities at yttrium positions, undergo major transformations due to the presence of calcium ions in the studied samples. The dependences of  $T_c$  and  $S(T = 300 \text{ K})$  on the content of these two impurities are qualitatively similar, while the dependences for  $Q(T = 300 \text{ K})$  are qualitatively different.

2. Based on quantitative analysis of the experimental data extracted, we have determined the values of all the main parameters for the energy spectrum and the charge-carrier system in the studied compounds and analyzed the nature and the mechanisms of their changes under increasing doping levels.

3. While the variations in the energy structure of the conduction band are qualitatively similar for doping with lanthanum and praseodymium, the influencing mechanisms of these impurities are fundamentally different. The effect from the La→Ba substitution is primarily related to the variation in oxygen content induced by this impurity, which was further reduced by introducing calcium ions into the lattice. The changing behavior of the praseodymium effect compared to the case of single doping is due to weakened hybridization between band states and praseodymium ion states, arising from the interaction of Pr ions with the Ca ions introduced into the lattice.

4. The differences in the concentration dependences of the electron mobility in  $Y_{0.85-x}Ca_{0.15}Pr_xBa_2Cu_3O_y$  and  $Y_{0.85}Ca_{0.15}Ba_{2-x}La_xCu_3O_y$  systems are related to quantitative differences in the influence that these impurities exert on the effective width of the conduction band and the degree of state localization within it. At the same time, the impurities considered have different (albeit rather weak) influences on the form of electron dispersion law in the  $YBa_2Cu_3O_y$  system.

5. We have established that the behavior detected for the dependences of the critical temperature on the impurity content in the given systems can be explained by analyzing the modification of the structure of the energy spectrum in the normal state that occurs upon doping, accounting for an additional peak in the density-of-states function and the effect of Fermi-level pinning in the region of this peak.

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