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Doping-induced variations of the Fermi level in calcium-containing Y-based HTSC and their influence on the critical temperature

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ABSTRACT

The superconducting and normal-state transport properties (resistivity, ρ, and thermopower, S) of three series of ceramic samples with compositions of $Y_{1-x}Ca_xBa_{1.5}La_{0.5}Cu_3O_y$ (x = 0–0.4), $Y_{0.85-x}Ca_{0.15}Pr_xBa_2Cu_3O_y$ (x = 0–0.3), and $Y_{0.85}Ca_{0.15}Ba_{2-x}La_xCu_3O_y$ (x = 0–0.3) have been investigated. The temperature dependences of the thermopower have been analyzed using a phenomenological narrow-band model. The mechanisms of the doping influence on the parameters of the band spectrum and charge-carriers system including the Fermi level position have been discussed. It has been demonstrated that the revealed features of the Fermi level behavior in the studied systems can be explained by the formation of an additional peak in the density-of-states function under calcium doping. The influence of the Fermi level shift under doping on the critical temperature in the studied systems is discussed.

1. Introduction

Notwithstanding the huge number of investigations of the high-temperature superconductors (HTSC) which have been carried out since their discovery over 25 years ago [1], the nature of the high-temperature superconductivity is not explained yet. Moreover, such issues as peculiarities of the energy spectrum structure of HTSC-materials in the normal state, the values of this spectrum and charge-carrier system parameters, mechanisms of their variations under changing sample compositions and influence on the critical temperature, T_c, value remain open and require additional studies. To answer these questions, the method of the experimental study and analysis of the temperature and concentration dependences of the transport coefficients, in particular, the thermopower, S, can be used, that was repeatedly demonstrated in cases of different HTSC-systems [2–10]. To realize this approach, it is necessary to use samples with systematically varied properties that can be obtained by introducing various nonisovalent impurities into the lattice resulting in variations of both the normal and superconducting states parameters.

Studies of yttrium-based HTSC have revealed the impurity whose influence on properties of this system is characterized by the presence of additional nontrivial features compared to that of other dopants. This impurity is calcium replacing yttrium in the $YBa_2Cu_3O_y$ lattice. The critical temperature value in calcium-containing systems changes differently with increasing calcium content in dependence on the cation and/or oxygen composition. In some systems calcium suppresses the superconductivity [11,12], in others it leads to a T_c restoration [11,12]. Besides, temperature and concentration dependences of the transport coefficients also demonstrate some specific features [11,13].

Earlier we have made an assumption that calcium doping introduces additional states in the conduction band of Y-based HTSC causing the appearance of an additional local peak in the density-of-state (DOS) function [11]. It allowed us to describe the thermopower modification in calcium-containing systems and to explain qualitatively the observed T_c variations [3]. Besides, this assumption was also successfully used by other authors for analyzing properties of the calcium-containing Y-based systems [14].

Let us note, that studying the transport properties of Y-based HTSC and analyzing them in the frame of a narrow-band model [2,3] we have found that in case of different types of doping there is the universal correlation between the effective conduction band width and the critical temperature. The reason for the existence of such a correlation is the impurity-induced modification of the energy spectrum leading to a decrease in the DOS value at the Fermi level [3]. However, in calcium-containing samples this correlation is violated that can be a consequence of the existence of calcium-induced peak in the DOS function. Indeed, if this peak in the energy spectrum of calcium-containing $YBa_2Cu_3O_y$ samples exists, it is reasonable to assume that the superconducting properties of such samples can be affected by its parameters, as well as by the position of the Fermi level relative to this peak. Thus determination

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of the Fermi level position in such samples and analysis of its variations under changing sample composition is of a great interest for revealing the mechanism of calcium influence on the superconducting and normal-state properties of Y-based HTSC-systems.

To obtain reliable data for our analysis we have chosen for investigations different calcium containing Y-based HTSC-systems, namely, $Y_{1-x}Ca_xBa_{1.5}La_{0.5}Cu_3O_y$ with a varied calcium content, as well as $Y_{0.85}Ca_{0.15}Ba_{2-x}La_xCu_3O_y$ with a fixed calcium content and a varied concentration of the second dopant. Besides, we have included in a comparative analysis the earlier obtained results for $Y_{0.85-x}Ca_{0.15}Pr_xBa_2Cu_3O_y$ system [15]. In the first system the calcium peak is supposed to appear with increasing doping, while in two last systems it should be already formed in samples with no Pr or La doping, so that an increase in praseodymium or lanthanum content is expected to result in a shift of the Fermi level relative to this peak position.

2. Samples and experimental details

Three series of ceramic samples with compositions of $Y_{1-x}Ca_xBa_{1.5}La_{0.5}Cu_3O_y$ (x = 0–0.4), $Y_{0.85-x}Ca_{0.15}Pr_xBa_2Cu_3O_y$ (x = 0–0.3), and $Y_{0.85}Ca_{0.15}Ba_{2-x}La_xCu_3O_y$ (x = 0–0.3) were prepared by the standard solid-state technique from initial oxides or carbonates with purity higher than 99%. Synthesis included three stages with intermediate regrinding, pressing into pellets, and annealing at temperatures of T = 900–950 °C for 24 h followed by slow cooling down to room temperature. In order to obtain more extensive information on the effect of the calcium doping, samples of the two last systems were investigated at different conditions of the oxygen subsystem. For this reason, $Y_{0.85}Ca_{0.15}Ba_{2-x}La_xCu_3O_y$ samples were additionally annealed in oxygen atmosphere for 10 h at T = 450 °C. 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 local values of the thermopower in various points on the sample surface at room temperature.

The resistivity, ρ, and the thermopower, S, were measured in the temperature range of $T = T_c$–300 K. For resistivity measurements we used 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 two ends of a sample about 2 K and then calculated by correcting for the absolute thermopower of copper. The error in determination of both transport coefficients values does not exceed 5%.

3. Experimental results

The $\rho(T)$ dependences for most of the studied samples show the typical for HTSC-materials behavior, with a T-linear drop of resistivity in the whole measured temperature range. The exceptions are two samples of the $Y_{1-x}Ca_xBa_{1.5}La_{0.5}Cu_3O_y$ system (with x = 0 and x = 0.05), for which the transition to a semiconductor-like dependence is observed at low temperatures, that is characteristic of the case of a high level of La-doping in $YBa_2Cu_3O_y$ [16]. Increasing Ca content in this system results in the transition to a metallic type of $\rho(T)$ dependence and decreasing ρ values. The values of resistivity at T = 300 K are small. Even for the most heavily doped samples they do not exceed 3 mΩ cm for $Y_{0.85-x}Ca_{0.15}Pr_xBa_2Cu_3O_y$, 4 mΩ cm for $Y_{0.85}Ca_{0.15}Ba_{2-x}La_xCu_3O_y$, and 8 mΩ cm for $Y_{1-x}Ca_xBa_{1.5}La_{0.5}Cu_3O_y$ systems. Thus, the resistivity data confirm a high quality of used ceramic samples.

The critical temperature values for all the studied samples determined from the $\rho(T)$ dependences as the mid-points of the superconducting transition are shown in Fig. 1. For $Y_{0.85-x}Ca_{0.15}Pr_xBa_2Cu_3O_y$ and $Y_{0.85}Ca_{0.15}Ba_{2-x}La_xCu_3O_y$ systems two regions on the

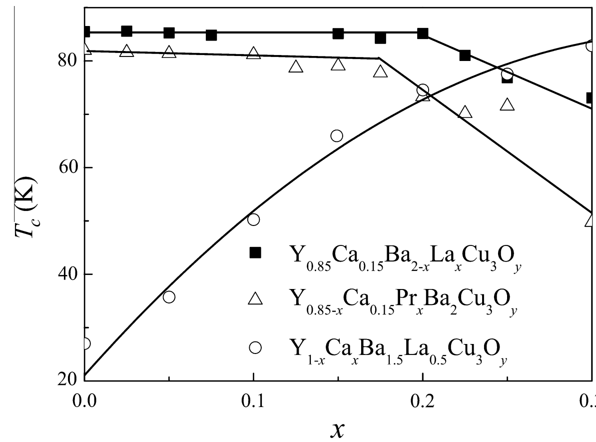

Fig. 1. Variation of the critical temperature with doping level in the studied systems.

$T_c(x)$ dependence can be clearly seen. At a low level of additional La or Pr doping (x = 0–0.175 for the $Y_{0.85-x}Ca_{0.15}Pr_xBa_2Cu_3O_y$ system and x = 0–0.2 for the $Y_{1-x}Ca_xBa_{1.5}La_{0.5}Cu_3O_y$ one) the critical temperature remains almost constant ($T_c \approx 80$ K for the first system and $T_c \approx 85$ K for the second one). Some difference in the T_c values for the discussed systems in this doping range is caused by a various overall level of the oxygen content in studied samples. Further increase in the doping level leads to the T_c suppression. In the $Y_{0.85}Ca_{0.15}Ba_{2-x}La_xCu_3O_y$ system the T_c value decreases rather slowly (down to T_c = 73 K at x = 0.3), while in the $Y_{0.85-x}Ca_{0.15}Pr_xBa_2Cu_3O_y$ system a stronger T_c fall is observed (as a result, T_c = 47.6 K at x = 0.3). Thus, $T_c(x)$ dependences observed 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 differ qualitatively from those in the $YBa_{2-x}La_xCu_3O_y$ [16] and $Y_{1-x}Pr_xBa_2Cu_3O_y$ [17,18] ones, i.e., a character of influence of La or Pr doping on the critical temperature in $YBa_2Cu_3O_y$ is strongly affected by the presence of Ca ions in the lattice. As for the $Y_{1-x}Ca_xBa_{1.5}La_{0.5}Cu_3O_y$ system, in this case the superconductivity is strongly suppressed by a preliminary La doping and restored rapidly with increasing Ca content (from T_c = 25 K for x = 0 to T_c = 82 K for x = 0.4). Thus, the doping dependence of the critical temperature in all the investigated systems containing Ca ions is characterized by some specific features evidencing an unusual Ca influence on the superconducting properties of Y-based HTSC.

The concentration dependences of the thermopower value at T = 300 K, $S_{300}(x)$, for the studied systems are presented in Fig. 2. Note, that the noticeable difference in the S_{300} values for $Y_{0.85}Ca_{0.15}Ba_{2-x}La_xCu_3O_y$ and $Y_{0.85-x}Ca_{0.15}Pr_xBa_2Cu_3O_y$ samples at small

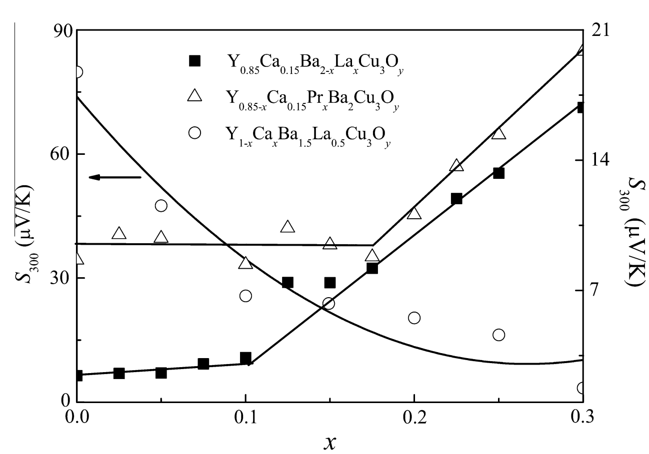

Fig. 2. Variation of the thermopower value at T = 300 K in the studied systems.