Thermopower in $Y_{1-x}Ca_xBa_{2-x}La_xCu_3O_y$ and $Y_{1-x}Ca_xBa_2Cu_{3-x}Co_xO_y$

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A systematic study of the thermopower behavior in codoped systems with compositions of $Y_{1-x}Ca_xBa_{2-x}La_xCu_3O_y$ ($0 \leq x \leq 0.4$) and $Y_{1-x}Ca_xBa_2Cu_{3-x}Co_xO_y$ ($0 \leq x \leq 0.3$) has been carried out. Both of these systems have been investigated in cases of a near-stoichiometric oxygen content and that reduced by vacuum annealing. For all the sample series increasing doping level was revealed to initiate a well-marked transformation of the $S(T)$ dependences which is noncharacteristic of the $YBa_2Cu_3O_y$ system in the case of different deviations from the stoichiometry. This transformation is assumed to be a consequence of a specific Ca influence on the band spectrum in the normal state. The thermopower at $T = 300$ K remains almost constant with x for $Y_{1-x}Ca_xBa_{2-x}La_xCu_3O_y$ while it increases gradually for $Y_{1-x}Ca_xBa_2Cu_{3-x}Co_xO_y$ in the case of a near-stoichiometric oxygen content and changes nonmonotonically after oxygen-reducing annealing. Comparing the results obtained for two different kinds of codoping we have concluded that in both of the investigated systems nonisovalent impurities placed at different lattice sites counterbalance the influence of each other on the charge balance in the lattice and properties of the charge-carrier system, but to a different extent. In the case of Ca/La doping the effect of total charge compensation is realized and this determines all the sample properties, while for the Ca/Co doping the compensation effect is accompanied by an additional mechanism affecting the properties of the charge-carrier system.
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I. INTRODUCTION

Substitutions for different native cations are extensively used to study the mechanism of superconductivity as well as the nature and properties of the normal state in high-temperature superconductors (HTSC's). Doping of the $YBa_2Cu_3O_y$ system by nonisovalent impurities affects strongly the charge-carrier system, leading to significant changes both of electronic and superconducting properties. Despite numerous data on this subject, the mechanism of some substitutions influence is still not completely understood. Besides, it is generally observed that any nonisovalent substitution leads to a deviation from the oxygen stoichiometry in different directions depending on the relationship between the valences of the dopant and the replaced element. In particular, substitutions for Cu(1) by transition metals (Fe, Co, Al) or for Ba by rare-earth elements result in increasing oxygen content.[1-5] Among all dopants calcium plays a special role because the substitution for Y^{3+} by Ca^{2+} is unique in that it induces decreasing oxygen content.[6-8] In any case, analyzing the results obtained on doped $YBa_2Cu_3O_y$, one should take into account two different factors affecting sample properties—the influence of incorporating the dopant itself and that of the changing oxygen content.

From this point of view, it is of considerable promise to study codoped systems such as Y(Ca)-Ba-Cu(M)-O (M = Fe, Co, Al) or Y(Ca)-Ba(La)-Cu-O, where one of dopants (Ca) has a valence less than the substituting element and, therefore, acts as a hole donor, while another one has a valence more than the corresponding native element and acts as a hole acceptor. In this case two kinds of impurities counterbalance the influence of each other on the charge balance in the system and, therefore, on the oxygen subsystem. As a result, in the case of an equal amount of two impurities (i.e., for the $Y_{1-x}Ca_xBa_2Cu_{3-x}M_xO_y$ and $Y_{1-x}Ca_xBa_{2-x}La_xCu_3O_y$ systems) the oxygen content remains almost constant with changing doping level,[9-11] which gives one a possibility to study directly the doping effect on properties of the $YBa_2Cu_3O_y$ system excluding (or, at least, minimizing) the influence of the oxygen content.

At the present the impact of codoping on properties of $YBa_2Cu_3O_y$ has attracted considerable interest, although data on some aspects of this influence are still lacking. The double-substitution effect was investigated in such systems as Y(Ca)-Ba-Cu(M)-O [where M = Fe,[12-14] Co,[9,15] Al (Refs. 10 and 16)], and Y(Ca)-Ba(La)-Cu-O.[11,17,18] Mainly, the structural and superconducting properties of these systems are discussed. The critical temperature was observed to drop very slowly due to the compensation effect in the case of an equal amount of two dopants,[9,10,11,15] and to increase if calcium is incorporated as the second dopant in a system with a fixed content of first impurity.[9,18,19] Concerning the transport properties in codoped systems, data on resistivity and, especially, thermopower are very few in number and nonsystematic. The question on the influence of codoping in the $Y_{1-x}Ca_xBa_2Cu_{3-x}M_xO_y$ and $Y_{1-x}Ca_xBa_{2-x}La_xCu_3O_y$ systems on the thermopower behavior is still open, while such information is very useful in order to study specific features of different impurities' influence on the superconducting and normal-state properties of $YBa_2Cu_3O_y$.

TABLE I. Lattice parameters and orthorhombic distortion of as-prepared $Y_{1-x}Ca_xBa_{2-x}La_xCu_3O_y$ samples as well as oxygen content before (y_1) and after (y_2) oxygen-reducing annealing.

x	a (Å)	b (Å)	$b-a$ (Å)	c (Å)	y_1	y_2
0.0	3.822	3.886	0.064	11.677	6.96	6.83
0.05	3.820	3.883	0.063	11.673	6.98	6.84
0.1	3.820	3.882	0.062	11.672	6.98	6.85
0.2	3.819	3.873	0.054	11.658	6.98	6.86
0.3	3.830	3.871	0.041	11.641	6.99	6.85
0.4	3.850	3.853	0.003	11.628	7.01	6.87

Thus the codoping effect in $YBa_2Cu_3O_y$ undoubtedly calls for further investigation. In this paper we first present the systematic data on the thermopower behavior in two codoped systems with compositions of $Y_{1-x}Ca_xBa_2Cu_{3-x}Co_xO_y$ ($x=0-0.3$) and $Y_{1-x}Ca_xBa_{2-x}La_xCu_3O_y$ ($x=0-0.4$). Besides, we have also studied the influence of an additional oxygen-reducing annealing on the normal-state and superconducting properties of these systems. Within a comparative analysis of all the results obtained both common peculiarities and specific features of two kinds of codoping are discussed.

II. SAMPLES AND EXPERIMENTAL DETAILS

Two series of ceramic samples with the composition of $Y_{1-x}Ca_xBa_{2-x}La_xCu_3O_y$ ($0\leqslant x\leqslant0.4$) and $Y_{1-x}Ca_xBa_2Cu_{3-x}Co_xO_y$ ($0\leqslant x\leqslant0.3$) were prepared by the standard solid-state powder processing technique. The high-purity powders of the respective oxides (Y_2O_3, CuO, Co_3O_4) or carbonates ($CaCO_3$, $BaCO_3$, and $LaCO_3$) were first dried and then mixed in required proportions and ground. The mixtures were calcined in air at 940 °C for 24 h, reground, pressed into pellets and sintered three times at 920–950 °C for 24 h with intermediate regrinding, followed by a slow cooling to room temperature. Finally, the pellets were heated in flowing oxygen at 450 °C for 10 h and furnace cooled down to room temperature.

X-ray-diffraction analysis was used to characterize the prepared samples and to determine the lattice parameters. All the samples were almost single phase, the foreign impurity level was found to be less than 1–2%. The lattice parameters for the $Y_{1-x}Ca_xBa_{2-x}La_xCu_3O_y$ and $Y_{1-x}Ca_xBa_2Cu_{3-x}Co_xO_y$ sample series are presented in Tables I and II, respectively. In agreement with results of

TABLE II. Lattice parameters and orthorhombic distortion of as-prepared $Y_{1-x}Ca_xBa_2Cu_{3-x}Co_xO_y$ samples.

x	a (Å)	b (Å)	$b-a$ (Å)	c (Å)
0.0	3.820	3.890	0.070	11.675
0.05	3.832	3.890	0.058	11.675
0.10	3.867	3.867	0	11.671
0.15	3.876	3.876	0	11.666
0.20	3.876	3.876	0	11.666
0.25	3.878	3.878	0	11.669
0.30	3.879	3.879	0	11.671

other authors,[11,15] an orthorhombic to tetragonal transition occurs near $x=0.4$ and 0.05–0.1 for Ca/La- and Ca/Co-doped samples, respectively (in the first case, all the samples are orthorhombic, but the sample with $x=0.4$ is close to being tetragonal).

Each prepared sample was cut into two parts, the first of them was used for measurements as as-prepared sample, whereas the second parts of all the samples were jointly annealed again at 450 °C for 2 h in a vacuum atmosphere in order to prepare oxygen-reduced samples. By such a way we have obtained four sample series with varied doping level at different conditions of the oxygen subsystem. To control the influence of last annealing on the sample composition we have determined the oxygen content in two series of $Y_{1-x}Ca_xBa_{2-x}La_xCu_3O_y$ samples using the iodometric titration technique with an accuracy of ±0.01–0.02. The results of these measurements are also presented in Table I. It can be seen that the oxygen content increases insignificantly with increasing doping level and due to the vacuum annealing the oxygen content in each sample was reduced by 0.13–0.14 per formula unit. The first fact clearly demonstrates that the effect of compensation of nonisovalent impurities' influence on the charge balance in the system is realized.

The resistivity measurements were performed by the standard four-probe low-frequency ac (20 Hz) method. The thermopower was measured relative to copper electrodes, its absolute value was calculated by correcting for the thermopower of copper. The temperature difference between the two ends of the sample was kept around 1–2 K throughout the measuring procedure and measured by a copper-constantan thermocouple mounted inside the copper electrodes. Both resistivity and thermopower measurements were performed in the temperature range of T_c–300 K.

III. RESULTS AND DISCUSSION

The temperature dependences of the resistivity demonstrate the usual behavior for Y-based high-T_c superconductors. For all as-prepared samples of both series, they are linear in the whole temperature range measured, with a decreasing slope of the $\rho(T)$ curves as the doping level increases [the ratio of $\rho(300$ K$)/\rho(100$ K$)$ decreases from 2.94 for undoped sample to 1.17 and 1.07 for maximally doped samples of $Y_{1-x}Ca_xBa_{2-x}La_xCu_3O_y$ and $Y_{1-x}Ca_xBa_2Cu_{3-x}Co_xO_y$ series, respectively]. In the case of oxygen-reduced samples, an increase in x leads to a gradual transition to a semiconducting type of $\rho(T)$ curve. Figure 1 shows the variation of the critical temperature, defined as the midpoint of resistive superconducting transition, with increasing doping level. It can be seen that for as-prepared samples the T_c value decreases slightly and nearly linearly when x increases. This drop of T_c is much slower compared to that for the case of appropriate single substitutions, which is in agreement with the data of Refs. 9, 11. It is necessary to note that despite different influences on T_c of the single doping of $YBa_2Cu_3O_y$ by La or Co the $T_c(x)$ dependences in the $Y_{1-x}Ca_xBa_{2-x}La_xCu_3O_y$ and $Y_{1-x}Ca_xBa_2Cu_{3-x}Co_xO_y$ systems coincide very closely.

As one can see in Fig. 1 an oxygen-reducing annealing affects in different ways two investigated systems. As a result, there is a drastic distinction between the $T_c(x)$ dependences in oxygen-reduced samples of the
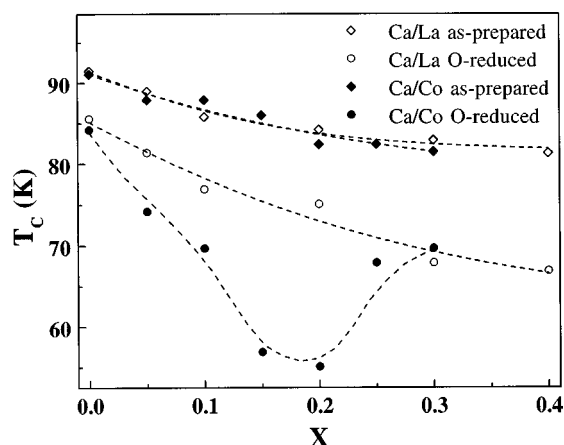
FIG. 1. Variation of the T_c value with doping level in $Y_{1-x}Ca_xBa_{2-x}La_xCu_3O_y$ and $Y_{1-x}Ca_xBa_2Cu_{3-x}Co_xO_y$ samples.

$Y_{1-x}Ca_xBa_{2-x}La_xCu_3O_y$ and $Y_{1-x}Ca_xBa_2Cu_{3-x}Co_xO_y$ series. In the first case, the T_c drop in oxygen-reduced samples becomes stronger than in the case of as-prepared ones, but remains monotonic. Contrary to this, the $T_c(x)$ dependence for the oxygen-reduced $Y_{1-x}Ca_xBa_2Cu_{3-x}Co_xO_y$ samples has two different regions. As x increases the critical temperature drops much more strongly compared to Ca/La-doped samples, then has a minimum at $x=0.2$, and finally increases drastically reaching at $x=0.3$ almost the same value as for the oxygen-reduced $Y_{1-x}Ca_xBa_{2-x}La_xCu_3O_y$.

The temperature dependences of the thermopower for all the investigated samples are shown in Figs. 2–5. Based on the presented data we will discuss hereafter the thermopower transformation with increasing dopant content in the case of two kinds of codoping.

For the as-prepared samples of the $Y_{1-x}Ca_xBa_{2-x}La_xCu_3O_y$ system the absolute value of ther-
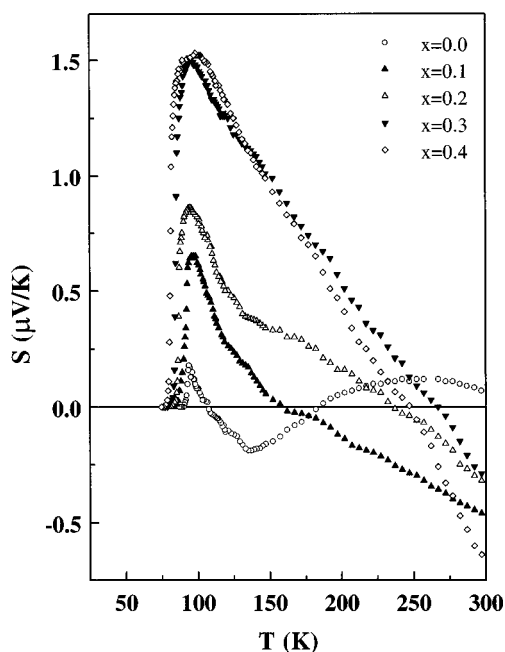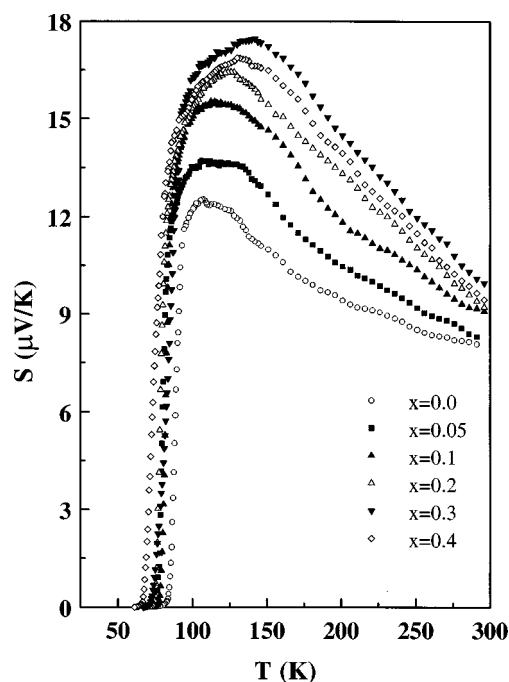

FIG. 3. Thermopower vs temperature for oxygen-reduced $Y_{1-x}Ca_xBa_{2-x}La_xCu_3O_y$ samples.

mopower changes very insignificantly with doping level (for example, the value of S at room temperature, $S_{300 K}$, is varied through a range of 1 $\mu V/K$). Obviously this is a consequence of the fact that $Ca^{2+} \rightarrow Y^{3+}$ and $La^{3+} \rightarrow Ba^{2+}$ substitutions counterbalance the influence of each other on the charge balance in the system, indicating, in addition, that in this case the compensation effect is totally realized. At the same time, the general view of $S(T)$ dependences undergoes a very essential modification, namely, an increasing doping level leads to a linearization of the $S(T)$ dependences and a

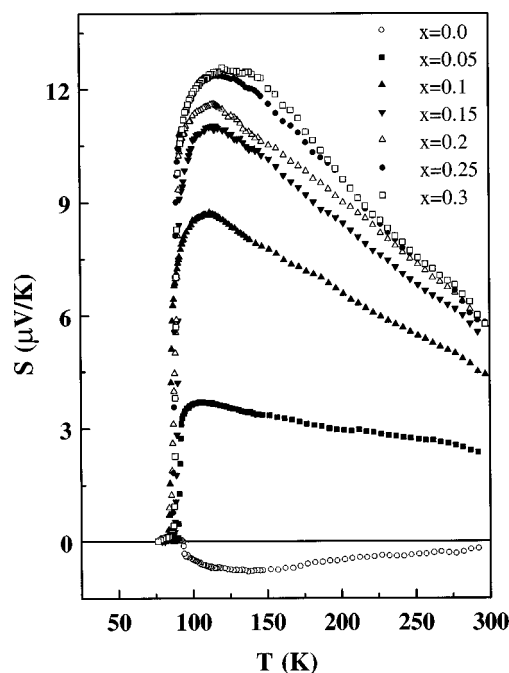FIG. 2. Thermopower vs temperature for as-prepared $Y_{1-x}Ca_xBa_{2-x}La_xCu_3O_y$ samples.

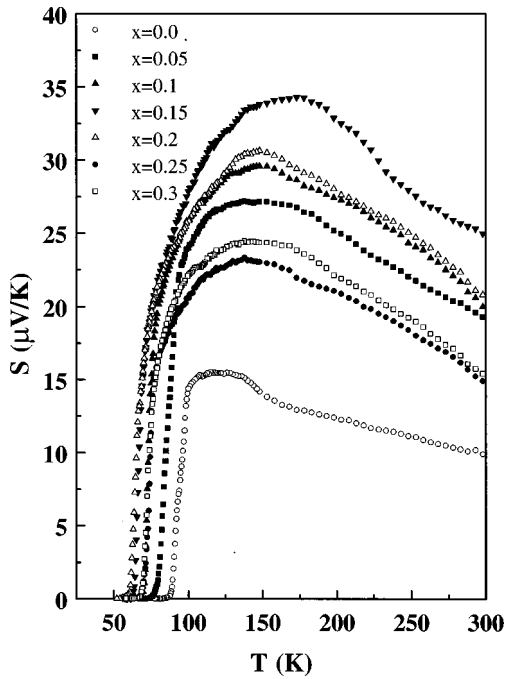FIG. 4. Thermopower vs temperature for as-prepared $Y_{1-x}Ca_xBa_2Cu_{3-x}Co_xO_y$ samples.

FIG. 5. Thermopower vs temperature for oxygen-reduced $Y_{1-x}Ca_xBa_2Cu_{3-x}Co_xO_y$ samples.

gradual rise of the $S(T)$ curves slope (see Fig. 2). For the oxygen-reduced series of $Y_{1-x}Ca_xBa_{2-x}La_xCu_3O_y$ the absolute value of the thermopower has increased, as a whole, by a value about 10 μV/K due to the deviation from the oxygen stoichiometry induced by vacuum annealing of the samples. As a result, the $S(T)$ dependences demonstrate the well-known peculiarity of the thermopower behavior in $YBa_2Cu_3O_y$ system, namely, the presence of a pronounced maximum at a temperature above the superconducting transition which shifts towards higher temperatures as dopant content increases (see Fig. 3). Note, that such a thermopower behavior is also characteristic of other HTSC cuprates in the case of different deviations from the stoichiometry resulting in an increasing thermopower value (see, for example, Ref. 20, and references therein). Nevertheless the specific features of the $S(T)$ dependences and their modification observed for as-prepared samples of the investigated system remain in the case of oxygen-reduced samples. In the latter case, an increase of dopant content is also accompanied, as one can see in Fig. 3, by a very slight increase of the $S_{300 K}$ value (from 8.1 μV/K to 9.5 μV/K as x goes from 0 to 0.4), an appearance of a T-linear region at the $S(T)$ dependences, and a significant rise of the slope of the $S(T)$ curves in this temperature region. The last phenomenon is well seen from the data in Fig. 3 if one compares the absolute value of thermopower at $T=290$ K and $T=140$ K [above a maximum on the $S(T)$ curves] for samples with different doping levels. For the undoped sample the thermopower value increases from 8.1 to 11.3 μV/K, while for the sample with $x=0.4$ it increases from 9.5 to 16.9 μV/K.

Now let us go to the thermopower results obtained for two $Y_{1-x}Ca_xBa_2Cu_{3-x}Co_xO_y$ series and compare them with those for the $Y_{1-x}Ca_xBa_{2-x}La_xCu_3O_y$ ones. It can be seen in Fig. 4 that in the case of as-prepared

$Y_{1-x}Ca_xBa_2Cu_{3-x}Co_xO_y$ samples increasing dopant content leads, contrary to the $Y_{1-x}Ca_xBa_{2-x}La_xCu_3O_y$ system, to a gradual increase of the $S_{300 K}$ value. This rise of $S_{300 K}$ is relatively slight and it is obvious that simultaneous incorporation of an equal amount of Ca and Co into the lattice affects the properties of $YBa_2Cu_3O_y$ in the opposite way although these two impurities do not totally counterbalance the influence of each other. An increase of the thermopower points to a stronger effect of cobalt doping. Note, that for the range of $x=0-0.15$ the $S_{300 K}$ value rises practically linearly with x, while on further increase of doping level it changes very insignificantly. At the same time it is clearly seen that, on the background of an increasing $S_{300 K}$ value, the $S(T)$ dependences for this system also take the specific features mentioned above. Indeed the gradual and strong rise of the slope of the $S(T)$ curves with x is well pronounced in the case of as-prepared $Y_{1-x}Ca_xBa_2Cu_{3-x}Co_xO_y$ samples. Even for samples with a high doping level that property can be easily seen in Fig. 4 [compare the view of $S(T)$ curves for the samples with $x=0.15$ and 0.3].

What is very interesting and unusual is the influence of vacuum annealing on the thermopower behavior in $Y_{1-x}Ca_xBa_2Cu_{3-x}Co_xO_y$ samples. We already noted above, that the $T_c(x)$ dependence for these samples becomes non-monotonic after that annealing. As shown in Fig. 5 the $S_{300 K}$ value for oxygen-reduced $Y_{1-x}Ca_xBa_2Cu_{3-x}Co_xO_y$ samples changes also nonmonotonically with x. When x runs from 0 to 0.1 the $S_{300 K}$ value goes up more strongly compared to the case of as-prepared samples of the same system. On further increase of doping level the thermopower value at room temperature falls from 25 μV/K at $x=0.1$ down to 15 μV/K at $x=0.3$. Thus, there is a qualitative correlation between the $S_{300 K}$ and T_c values despite their nonmonotonic dependence on doping level. Note that for both $Y_{1-x}Ca_xBa_2Cu_{3-x}Co_xO_y$ series a maximum of the $S(T)$ curves at low temperatures is well pronounced and shifts towards higher temperatures with increasing dopant content, as well as in the case of oxygen-reduced $Y_{1-x}Ca_xBa_{2-x}La_xCu_3O_y$ samples.

Thus there are several points in the results obtained on which to focus one's attention. First, we have observed both common peculiarities and specific features of codoping by Ca/La and Ca/Co on the thermopower behavior in $YBa_2Cu_3O_y$. On the one hand, for both of these impurities' combinations an increasing doping level initiates the appearance of additional peculiarities of the $S(T)$ dependences. Those are the existence of an extended region of a T-linear increase of the thermopower with decreasing temperature and a gradual increase of the $S(T)$ curves slope in this region as doping level increases. Such a property looks to be very unusual for the thermopower in the $YBa_2Cu_3O_y$ system and the possible reasons for this behavior will be briefly discussed hereafter. On the other hand, two kinds of codoping we investigated differ in their influence on the $S_{300 K}$ value. Indeed in the case of $Y_{1-x}Ca_xBa_{2-x}La_xCu_3O_y$ samples, both as-prepared and oxygen-reduced, the $S_{300 K}$ value remains nearly unchanged with x, whereas for the $Y_{1-x}Ca_xBa_2Cu_{3-x}Co_xO_y$ ones it rises gradually for as-prepared samples and changes nonmonotonically but relatively distinctly for oxygen-reduced ones. Nevertheless in both these cases the $S_{300 K}$ value changes, as a whole, insig-

nificantly compared to the case of single substitutions by La for Ba or by Co for Cu. In the last two cases the thermopower value rises drastically with increasing doping level from a value close to 0 μV/K for an undoped sample up to 27 μV/K for $YBa_{1.6}La_{0.4}Cu_3O_y$ (Ref. 21) or 60 μV/K for $YBa_2Cu_{2.7}Co_{0.3}O_y$.[22] Obviously, such a property of the thermopower in codoped systems is a result of the well-known compensation effect of nonisovalent substitutions in Cu(1) or Ba and Y sites on the charge balance in the lattice. The impurities with a higher (Co^{3+} and La^{3+}) or lower (Ca^{2+}) valence compared to substituted elements affect, in the opposite way, the properties of the system such as the oxygen content, charge-carrier concentration, and, as a result, the thermopower value.

Besides summarizing the experimental data, we would like to note that for all the sample series studied there is a correlation between the values of T_c and $S_{300 K}$. For three of them, namely, $Y_{1-x}Ca_xBa_{2-x}La_xCu_3O_y$ with different oxygen content and $Y_{1-x}Ca_xBa_2Cu_{3-x}Co_xO_y$ with near-stoichiometric oxygen content, an increasing $S_{300 K}$ value is accompanied by a gradual decrease of the T_c value, whereas for oxygen-reduced $Y_{1-x}Ca_xBa_2Cu_{3-x}Co_xO_y$ samples a minimum of the $T_c(x)$ dependence and a maximum of the $S_{300 K}(x)$ one take place at the same level of doping.

Thus the comparison of the results obtained for $Y_{1-x}Ca_xBa_{2-x}La_xCu_3O_y$ and $Y_{1-x}Ca_xBa_2Cu_{3-x}Co_xO_y$ shows clearly that, despite impurities placed in different lattice sites resulting in a realization of the charge-compensation effect in both these systems, the cases of $YBa_2Cu_3O_y$ doping by either Ca and La or Ca and Co differ from each other by the extent of this compensation. In the latter case an increasing doping level affects more strongly the thermopower and the properties of the charge-carrier system, as a whole.

Going to a brief discussion of results obtained, we will first focus on the common peculiarities of the transformation of the $S(T)$ dependences under codoping which were observed for all the investigated series. This is the appearance of a T-linear region on the $S(T)$ curves accompanied by a rise of the $S(T)$ slope with x. As a result, with increasing doping level the view of the $S(T)$ dependences for investigated systems becomes more and more like that characteristic of other HTSC materials, excluding the case of the $La_{2-x}Sr_xCuO_4$ system. To explain this fact, different assumptions can be used. Some of authors discussing the thermopower modification in $YBa_2Cu_3O_y$ suggest that the most likely reason for this is a change of relation between the chain and plane contributions to the thermopower.[23,24] The plane contribution gives a negative slope of $S(T)$, while the chain contribution has a large positive one.[23] In the framework of this consideration the chain contribution is suppressed when the CuO chains are either strongly deoxygenated or disordered due to doping. This leads to the above thermopower modification, i.e., to a linear decrease of S with increasing temperature. At the same time, Cohn et al.[25] suggest that the temperature-independent thermopower behavior at high temperatures for $YBa_2Cu_3O_y$ with $y \approx 7$ is associated with electronic transport along the chains which gives a large contribution to the thermopower for near-stoichiometric composition.

Such a picture looks to be quite reasonable but, in this respect, we would like to focus attention on the following results. First, if one compares the $S(T)$ dependences for the samples of the oxygen-reduced series presented here (see Figs. 3, 5) with data on oxygen-reduced $YBa_2Cu_3O_y$ taken for the same $S_{300 K}$ value,[20,26] it can be clearly seen that in the first case the slope of $S(T)$ dependences is much larger that in the second one, while the oxygen content in corresponding $YBa_2Cu_3O_y$ samples is significantly less, i.e., the chains are more deoxygenated. Second, it is known that even for strongly deoxygenated $YBa_2Cu_3O_y$ samples the thermopower becomes temperature independent at high temperatures although this region shifts to higher temperatures.[27–29] Moreover, we have earlier observed[30] that for $Bi_2Sr_2Ca_{1-x}Nd_xCu_2O_y$ ($x=0-0.5$) samples the thermopower at $T>620 K$ also demonstrates the temperature-independent behavior. This clearly points that such a $S(T)$ peculiarity is common for Y- and Bi-based HTSC's and cannot be associated with the chain contribution.

All the facts listed above lead one to doubt the interpretation of $S(T)$ transformation in $YBa_2Cu_3O_y$ under doping in terms of changing chain contribution. We believe that there is an alternative possibility for explaining the results obtained for our codoped samples. Keeping in mind the fact that observed $S(T)$ modification is not intrinsic for $YBa_2Cu_3O_y$ in the case of different kinds of deviation from the stoichiometry (including the case of single substitution for Ba by La and for Cu by Co), we would like to call attention to the following results. We have previously observed that doping by calcium in the case of either $Y_{1-x}Ca_xBa_2Cu_3O_y$ (Ref. 21) or $Y_{1-x}Ca_xBa_{1.5}La_{0.5}Cu_3O_y$ and $Y_{1-x}Ca_xBa_2Cu_{2.75}Co_{0.25}O_y$ (Ref. 11) systems affects the thermopower temperature dependences in the same way. Note, that analogous result was obtained by Zelenay et al.[31] in studies of the Ca effect on the thermopower in $L_{1-x}Ca_xBa_2Cu_{2.9}Ga_{0.1}O_y$ ($L=$Nd, Dy). The data presented here differ advantageously in that the absolute value of the thermopower in each series changes insignificantly with increasing doping level due to the compensation effect and, as a result, specific features of the $S(T)$ transformation are most conspicuous. Common to all the above-listed systems including the ones investigated in this paper is the incorporation of calcium into the lattice. Thus there is a good reason to conclude that it is calcium that is responsible for the specific $S(T)$ transformation described above.

If so, the results obtained can be qualitatively understood assuming that Ca doping gives rise to the appearance of some additional peculiarities in the band spectrum of $YBa_2Cu_3O_y$ in the vicinity of the Fermi level, affecting the normal-state transport properties of any Ca-doped samples. The nature of these peculiarities, as well as validity of such an assumption, invite further investigation.

Another question we would like to discuss is possible reasons for a nonmonotonic change of the thermopower and T_c in the case of oxygen-reduced $Y_{1-x}Ca_xBa_2Cu_{3-x}Co_xO_y$ samples. Obviously the case of Ca/Co doping is characterized by a specific influence on $YBa_2Cu_3O_y$ properties, compared to the Ca/La doping, the reason for which cannot be completely understood now. In this connection one can mention the data obtained by Zhao et al.[15] They argue that copper cations with the valence of 3+ appear in the $Y_{1-x}Ca_xBa_2Cu_{3-x}Co_xO_y$ system starting from $x=0.1$. Note

that an additional transformation of the lattice (a nonmonotonic dependence of the c parameter observed both by us and Zhao *et al.*[15]) can be considered as indirect evidence for such a possibility. If so, despite the equal amounts of donor Ca^{2+} and acceptor Co^{3+} in the system the influence of impurities placed at different sites becomes nonequivalent and the charge balance in the lattice is disturbed because of additional Cu^{3+} ions. This effect could be a reason for a slighter change of the thermopower value at $x>0.1$ in as-prepared samples. Under vacuum annealing (oxygen-reduced samples) the presence of Cu^{3+} ions can initiate an additional redistribution of the oxygen atoms that affects the $S_{300\,K}$ and T_c values resulting in their nonmonotonic dependence on the doping level. Certainly, such an assumption can be considered only as a qualitative attempt to explain the obtained results and further investigations are needed to clarify the question on the specific effect of the Ca/Co doping on the $YBa_2Cu_3O_y$ properties. At the present we can state with confidence that, despite in both investigated systems nonisovalent impurities compensate the effect of each other on the charge balance in the lattice and properties of charge-carrier system, their influence is qualitatively different. In the case of Ca/La doping the effect of total compensation is realized inducing no charge redistribution and thus all the sample properties are determined by this effect. On the other hand, the Ca/Co doping is followed by an additional mechanism affecting the sample properties which calls for further investigation.

IV. CONCLUSIONS

In conclusion, we have first presented the systematic data on the thermopower behavior for two codoped systems with compositions of $Y_{1-x}Ca_xBa_{2-x}La_xCu_3O_y$ and $Y_{1-x}Ca_xBa_2Cu_{3-x}Co_xO_y$ with varied doping level and different conditions of the oxygen subsystem. The obtained results can be summarized as follows.

The $S_{300\,K}$ value in the case of near-stoichiometric oxygen content does not change with x for Ca/La doping and increases for Ca/Co doping. An oxygen-reducing annealing affects the $S_{300\,K}$ and T_c values in two investigated systems in a different way, resulting in their nonmonotonic dependence on x in the case of $Y_{1-x}Ca_xBa_2Cu_{3-x}Co_xO_y$.

For all the investigated sample series increasing doping level initiates a well-marked transformation of the $S(T)$ dependence resulting in the appearance of a region of T-linear thermopower decrease with temperature accompanied by a gradual rise of the $S(T)$ curves slope. This unusual thermopower behavior is assumed to be induced by calcium, the incorporation of which in $YBa_2Cu_3O_y$ leads to a modification of the band spectrum in the normal state.

The impurities placed at the Y site and either Ba or Cu(1) sites counterbalance the influence of each other on the absolute value of the thermopower but to a different extent in the cases of doping for Ba by La or for Cu by Co. In the case of Ca/La doping the effect of total compensation of impurities' influence determines all the sample properties, while for the Ca/Co doping an additional mechanism affecting the oxygen sublattice and charge-carrier system is realized.

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