Physics of Complex Systems, 2020, vol. 1, no. 4
www.physcomsys.ru

Condensed Matter Physics. Physics of Transport Phenomena in Condensed Matter

UDC 538.935 DOI: 10.33910/2687-153X-2020-1-4-142-149

The calcium effect on the thermopower, critical temperature and charge-carrier system parameters in the $Y_{0.75-x}Ca_xPr_{0.25}Ba_2Cu_3O_y$ HTSC-system

E. V. Gasumyants✉[1, 2]

[1] Peter the Great St. Petersburg Polytechnic University, 29 Polytechnicheskaya Str., Saint-Petersburg 195251, Russia
[2] Herzen State Pedagogical University of Russia, 48 Moika Emb., Saint Petersburg 191186, Russia

Author
Vitaliy E. Gasumyants, ORCID: 0000-0002-5306-6738, e-mail: vgasum@yandex.ru

For citation: Gasumyants, V. E. (2020) The calcium effect on the thermopower, critical temperature and charge-carrier system parameters in the $Y_{0.75-x}Ca_xPr_{0.25}Ba_2Cu_3O_y$ HTSC-system. *Physics of Complex Systems*, 1 (4), 142–149. DOI: 10.33910/2687-153X-2020-1-4-142-149

Received 19 October 2020; reviewed 1 November 2020; accepted 1 November 2020.

Abstract. Superconducting properties and thermopower temperature dependences for two series of ceramic samples with $Y_{0.75-x}Ca_xPr_{0.25}Ba_2Cu_3O_y$ ($x = 0$–0.25) compositions are experimentally investigated. Thermopower temperature dependences are analysed using the phenomenological narrow-band model. The normal state energy spectrum and the charge-carrier system parameters including the Fermi level position are determined and the doping influence on their value is discussed. It is shown that the Fermi level position in $Y_{0.75-x}Ca_xPr_{0.25}Ba_2Cu_3O_y$ samples is determined by its pinning inside a local peak in the density-of-states function formed due to increasing calcium content. The influence of the observed normal-state energy spectrum modification on the critical temperature in the studied system is discussed.

Keywords: high-temperature superconductors, calcium doping, critical temperature, thermopower, narrow-band model, normal-state energy spectrum, Fermi level.

Introduction

The high-temperature superconductors (HTSC) were discovered more than 30 years ago; however, the electron pairing mechanism in these materials which results in anomaly high critical temperature values, T_c, is still not determined. Although different high-T_c superconductivity mechanisms have been proposed, none of them can be considered generally accepted. However, not only the superconducting properties of these materials seem unusual. Many HTSC properties not related directly to superconductivity and observable in the normal state are also not typical of standard objects in the solid state physics; for example, the electron transport phenomena. The characteristic temperature dependences of resistivity, ρ, thermopower, S, Hall, R_H and Nernst, Q, coefficients make it impossible to describe and quantitatively analyse them based on the classical electron transport models developed for metals or semiconductors (for early reviews, see Gasumyants 2001; Iye 1992; Kaiser, Ucher 1991; Ong 1990). It is obviously due to the structure of the normal-state energy spectrum in HTSC, but its main parameters remain to be not defined. This is why different models were suggested to explain the experimental results on the electron transport in HTSC-materials. One of them is the narrow-band model based on the assumption that the HTSC energy spectrum contains a narrow peak of the density-of-states function (Gasumyants et al. 1995). Unlike others, this model makes it possible to describe all the behaviour features of the four transport coefficients using a common parameter set with a clear physical meaning. It can be used to determine certain energy spectrum and charge-carrier system parameters by analysing the experimental results regarding the thermopower temperature dependences in samples of various composition, and thus to investigate the parameter modification depending on the doping type and level.

Studies on yttrium-based HTSC revealed the impurity that gives the system additional nontrivial properties not caused by other dopants. This impurity is calcium that replaces yttrium in the $YBa_2Cu_3O_y$ lattice (Jirak et al. 1988; Manthiram et al. 1988; Tokiwa et al. 1988). The effect of calcium doping on the T_c value depends on the initial sample composition. In the case of the close-to-stoichiometric $YBa_2Cu_3O_y$, calcium suppresses its superconductivity (Fisher et al. 1993; McCarron III et al. 1989; Parise, McCarron III 1989); however, in samples where the critical temperature was preliminary decreased by other factors (the oxygen deficit or the second introduced impurity), calcium can lead to the superconductivity restoration (Awana et al. 1996; Gasumyants et al. 1994; Gasumyants et al. 1998; Gasumyants, Elizarova, Vladimirskaya et al. 2000; Komarova et al. 2013; Liu et al. 1990; McCarron III et al. 1989; Martynova, Potapov et al. 2011; Parise, McCarron III 1989; Vladimirskaya et al. 1995). Besides, calcium doping makes the thermopower temperature dependences acquire additional properties (most pronounced in double-substituted systems) that are not observed if other substitutions are used (Elizarova, Gasumyants 1999; Gasumyants 2001; Gasumyants et al. 1998; Gasumyants, Elizarova, Patrina 2000; Ghorbani et al. 2003). Therefore, calcium-containing $YBa_2Cu_3O_y$ system samples are very intriguing objects to study.

This paper presents the results of the study of the calcium doping effect on the critical temperature value and the thermopower behaviour in $Y_{0.75\text{-}x}Ca_xPr_{0.25}Ba_2Cu_3O_y$ samples.

Samples and experiment

Ceramic samples with $Y_{0.75\text{-}x}Ca_xPr_{0.25}Ba_2Cu_3O_y$ ($x = 0–0.25$) compositions were prepared by the standard solid-state technique from initial oxides or carbonates with purity higher than 99%. Their synthesis included three stages with intermediate regrinding and was performed in air. Thus, the initial sample series (series 1) was made. In order to obtain more extensive information on the calcium doping effect, we also studied an additional sample series of the same cation compositions that differs in conditions of the oxygen subsystem. Samples in this series (series 2) had maximum oxygen saturation due to their additional annealing in oxygen flow at $T = 450$°C for 2 h.

X-ray diffraction analysis showed that all the samples were almost single phase with foreign impurities not exceeding 1–2 %. The sample homogeneity was controlled by measuring the thermopower local values in various points on the sample surface at room temperature.

The resistivity and the thermopower were measured in the $T = T_c$–300 K temperature range. For resistivity measurements, the standard four-probe low-frequency ac ($f = 20$ Hz) method was used. The thermopower was measured by a differential method relative to copper electrodes at the temperature difference between the two ends of a sample about 2 K and then calculated by correction for the absolute copper thermopower. The measurement error for both transport coefficients did not exceed 5%.

Experimental results

The $\rho(T)$ dependences for all the studied samples demonstrate a T-linear resistivity decrease with decreasing temperature in the whole measured temperature range that is typical of most $YBa_2Cu_3O_y$ system HTSC samples, excluding very strong doping cases (Gasumyants 2001; Kaiser, Ucher 1991). The critical temperature values determined by the resistive measurements are shown in Figure 1.

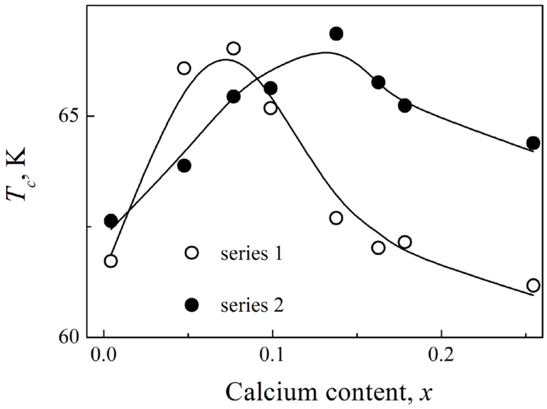

Fig. 1. Critical temperature vs. calcium content in $Y_{0.75\text{-}x}Ca_xPr_{0.25}Ba_2Cu_3O_y$ samples

The $T_c(x)$ dependences for both studied samples series are non-monotonic. When the calcium content is low, the critical temperature increases, but it starts to decrease with further increase in x. Besides, the position of the maximum on the $T_c(x)$ curve depends on the oxygen subsystem condition. For series 2 with a higher oxygen content, this maximum moves to a higher calcium doping level.

The $S(T)$ dependences measured for series 2 are shown in Figure 2. They are typical for calcium-containing samples of the $YBa_2Cu_3O_y$ system. The thermopower demonstrates a maximum at a temperature well above T_c whose position depends on the specific calcium content. Further increase in temperature results in a linear thermopower decrease. It should be noted that the latter is the distinguishing feature of the thermopower behaviour when calcium ions are present in the $YBa_2Cu_3O_y$ lattice (as for other impurities, the thermopower becomes almost temperature-independent at high temperatures) (Gasumyants, Martynova 2017). Nevertheless, there is an additional characteristic feature in the $S(T)$ modification under calcium doping in the studied system. In most systems, increased calcium content causes a T-linear region to appear on the $S(T)$ curve and results in a gradual increase in the $S(T)$ slope (Gasumyants, Martynova 2017). As seen in Figure 2, the $S(T)$ slope in the $Y_{0.75-x}Ca_xPr_{0.25}Ba_2Cu_3O_y$ system remains almost unchanged. This indirectly confirms our earlier conclusion that, if Ca and Pr are simultaneously introduced into the lattice, their influence on the $YBa_2Cu_3O_y$ properties cannot be considered a simple summation of their individual influences because calcium and praseodymium ions interact with each other (Martynova, Gasumyants 2006; Martynova, Gasumyants, Babichev 2011).

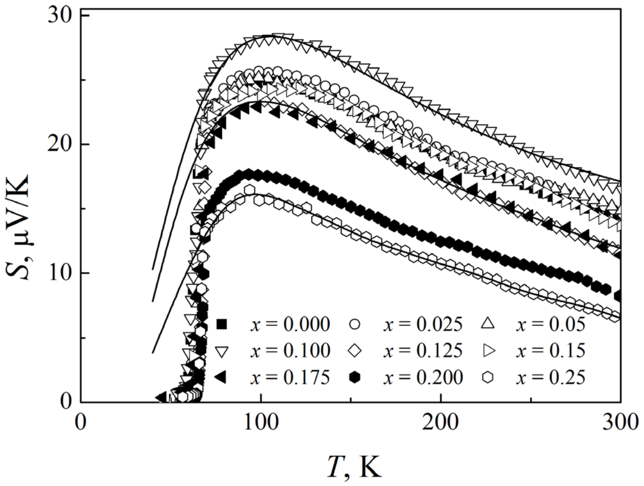

Fig. 2. Thermopower temperature dependences in oxygen-saturated $Y_{0.75-x}Ca_xPr_{0.25}Ba_2Cu_3O_y$ samples (series 2). Symbols are the experimental data; lines are the calculation results according to the narrow-band model

Series 1 experimental $S(T)$ dependences are analogous in quality to those of series 2, and thus demonstrate all the properties described above. The only difference is the absolute thermopower value. Since the oxygen deficit is known to result in increased thermopower value, the S values at T = 300 K change from 6.6 to 16.4 mV/K for series 2 and from 14.2 to 20.3 mV/K for series 1.

Discussion

The experimental $S(T)$ dependences were analysed within the narrow-band model (for the detailed model description see Gasumyants et al. 1995). Briefly, this approach is based on the assumption that the HTSC energy spectrum contains a single narrow band responsible for the conduction process or a sharp peak in the density-of-states function located near the Fermi level position. In this case, the simplest rectangular approximations can be used for the density-of-states, $D(\varepsilon)$, differential conductivity, $\sigma(\varepsilon)$, and Hall conductivity functions. Due to both the energy dependence character of these functions and a possible charge-carriers localisation at the band edges, the approximating rectangles should have rather different widths (Gasumyants et al. 1995). Besides, taking into account a possible $D(\varepsilon)$ function asymmetry, the centres of rectangles approximating the $D(\varepsilon)$ and $\sigma(\varepsilon)$ functions should be shifted relative to each other. Within such approximations, the energy structure of the narrow conduction band is characterised by three parameters — W_D is the total effective bandwidth, W_σ is the effective width of the delocalised states interval and b is the band asymmetry degree. The fourth needed parameter is the band filling with electrons determined as $F = n/N$, where n is the total number of electrons in the band and N is the total number of the band states.

Based on the model-independent kinetic integrals and the above approximations for the $D(\varepsilon)$ and $\sigma(\varepsilon)$ functions, the following analytical expression is easily derived for the thermopower temperature dependence:

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

where:

$$\mu^* \equiv \mu / k_B T = \ln\frac{\sinh\left(FW_D^*\right)}{\sinh\left[\left(1-F\right)W_D^*\right)]} - 2bW_D^*,$$

$W_D^* \equiv \dfrac{W_D}{2k_BT}$, $W_\sigma^* \equiv \dfrac{W_\sigma}{2k_BT}$, k_B is the Boltzmann constant, e is the elementary change, μ is the electrochemical potential.

As shown by Gasumyants (2001) and Gasumyants et al. (1995), it is possible to obtain the calculated curves that describe the thermopower behaviour for HTSC samples with varied composition using different model parameter values in the above formulae. Fitting the experimental $S(T)$ curves obtained for different samples into the above equation determines the model parameter values characterising the energy spectrum structure in each sample.

The described approach was used to analyse the experimental results and allowed us to achieve a good agreement between the experimental and calculated $S(T)$ dependences for all the studied samples. To illustrate this agreement, several calculated $S(T)$ curves are shown in Figure 2 together with the experimental results. The observed variations in the energy spectrum and charge-carrier system parameters in the $Y_{0.75-x}Ca_xPr_{0.25}Ba_2Cu_3O_y$ system with increasing calcium content are discussed below.

Firstly, the band asymmetry degree for studied samples in series 1 and 2 with the same calcium content is almost equal. As the calcium content increases, the b value changes linearly and the $b(x)$ dependence corresponds very well to the $b \approx -0.12 \cdot x$ relationship characteristic of other yttrium system calcium-containing samples (Gasumyants, Elizarova, Vladimirskaya et al. 2000; Gasumyants, Martynova 2017). Obviously, this is because it is calcium that causes the band asymmetry in $YBa_2Cu_3O_y$ to appear due to additional states introduced into the conduction band.

Figure 3 shows the effective conduction bandwidth variation in two $Y_{0.75-x}Ca_xPr_{0.25}Ba_2Cu_3O_y$ sample series. It shows that the bandwidth decreases almost linearly as the calcium content increases, and the W_D value for samples in series 1 are always higher that for corresponding samples in series 2. Contrary to the studied system, if there is a single Ca→Y substitution in the $YBa_2Cu_3O_y$ system, calcium doping results in a slight band broadening (Gasumyants 2001; Gasumyants, Martynova 2017). To explain the obtained results, it is necessary to take into account the following. Firstly, single praseodymium doping leads to a strong increase in the W_D value due to hybridisation of Pr ion and band states

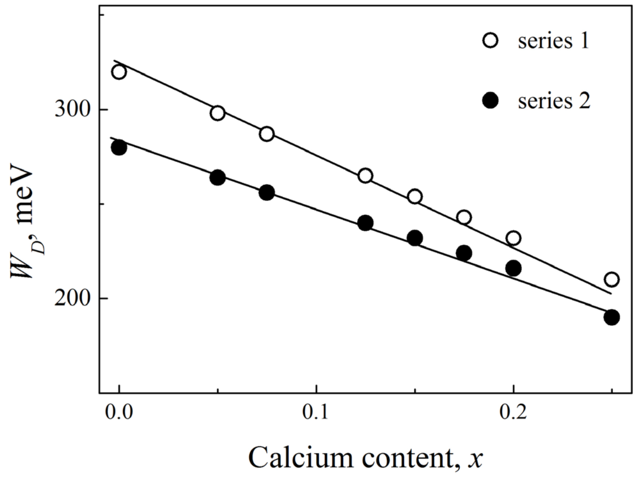

Fig. 3. Effective bandwidth vs. calcium content in $Y_{0.75-x}Ca_xPr_{0.25}Ba_2Cu_3O_y$ samples

(Gasumyants et al. 1997) that results in high W_D values for initial samples in both series. Secondly, increasing oxygen deficit also leads to the W_D rise, hence higher bandwidth values in series 1. Thirdly, as mentioned earlier, Ca and Pr ions interact when simultaneously introduced into the lattice. As a result, the Pr effect on the band structure gradually weakens as calcium content increases, causing the observed band narrowing in the studied system. Thus, the obtained $W_D(x)$ dependences can be explained consistently taking into account the specific features of the influence of the studied impurities on the energy spectrum structure.

Figure 4 shows the variation of the band filling with electrons in two $Y_{0.75-x}Ca_xPr_{0.25}Ba_2Cu_3O_y$ sample series. In general, the $F(x)$ dependences for both sample series demonstrate a tendency to a linear decrease. This is characteristic of calcium doping because it increases the total number of states in the band by introducing additional states, and therefore decreases the degree to which it is filled with electrons (Gasumyants, Elizarova, Vladimirskaya 2000; Gasumyants, Martynova 2017). However, the $F(x)$ dependence in both sample series reaches a plateau at x = 0.125–0.15 for oxygen-deficient samples and x = 0.075–0.175 for oxygen-saturated ones. In order to clarify the reason underlying this fact, it seems reasonable to analyse the Fermi level movement in the studied systems.

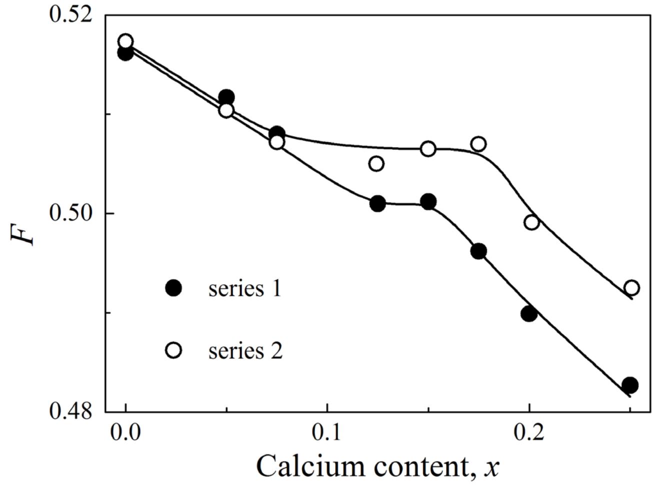

Fig. 4. The band filling with electrons vs. calcium content in $Y_{0.75-x}Ca_xPr_{0.25}Ba_2Cu_3O_y$ samples

According to our analysis (Komarova, Gasumyants 2010), the low-temperature Fermi level position relative to the middle of the conduction band can be calculated as $E_F = (F - ½)W_D - bW_D$. Calculation results are shown in Figure 5. The Fermi level remains almost constant in a wide calcium doping range, namely, at x = 0–0.2 and x = 0–0.175 for oxygen-deficient and oxygen-saturated series, respectively. As mentioned earlier, calcium ions form an additional peak in the $D(\varepsilon)$ function. Two investigated sample series differ very slightly in the oxygen content; therefore, we can suppose that for the initial samples in both series the Fermi level is located in the energy range where the local calcium peak in the $D(\varepsilon)$ function will be formed. If so, since a calcium-induced peak becomes more pronounced as x increases, the Fermi level is pinned inside this peak. When calcium content is high, E_F moves outside this peak and shifts to lower energies. A minor difference in calcium content at which the pinning effect is observed in different sample series is explained by the influence of the slightly changing oxygen content on the starting (in calcium-free samples) Fermi level position in these two series. It should be noted that the Fermi level in the pinning range (4–6 meV, see Fig. 5) corresponds well to our previously drown conclusion that calcium-induced peak is located in the energy range 2–8 meV from the band middle (Komarova et al. 2013).

Thus, we can conclude that such properties as absolute thermopower and critical temperature values should be influenced by the Fermi level pinning inside the forming calcium-induced peak in the density-of-states function.

Finally, let us discuss the critical temperature variation in the investigated system. According to our previous results, the critical temperature in doped $YBa_2Cu_3O_y$ is always affected by changes in the density-of-states function value at the Fermi level, $D(E_F)$. The main reason for these changes is

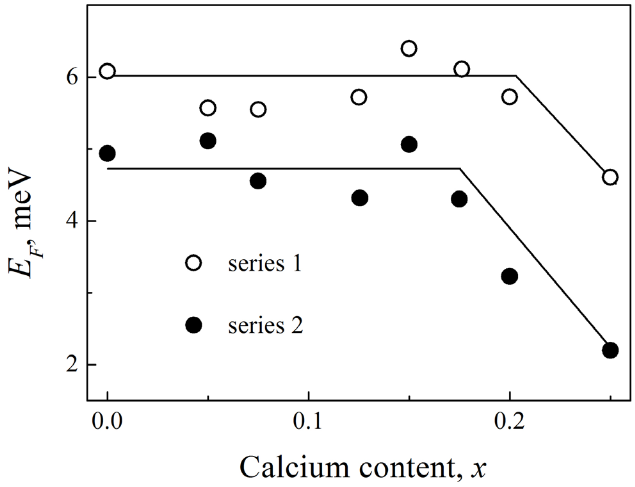

Fig. 5. Fermi level position vs. calcium content in $Y_{0.75-x}Ca_xPr_{0.25}Ba_2Cu_3O_y$ samples

an impurity-induced variation of the conduction band width. It is confirmed by the fact that T_c and W_D in doped $YBa_2Cu_3O_y$ samples for most doping types fall well on the universal $T_c(W_D)$ correlation dependence (Gasumyants 2001). However, in general, the $D(E_F)$ value in doped samples can be affected by several factors. In the $Y_{0.75-x}Ca_xPr_{0.25}Ba_2Cu_3O_y$ system, it is necessary to take into account the following possible reasons for the $D(E_F)$ change: (1) the energy spectrum modification induced by the Pr introduction into the lattice; (2) Pr and Ca ions interaction; (3) the direct calcium effect on the energy spectrum structure, i.e., the formation of the Ca-induced peak in the $D(\varepsilon)$ function; (4) the Fermi level position variation under doping including the effect of E_F pinning inside the forming Ca-induced peak. Clearly, it is rather impossible to estimate quantitatively the resultant effect of all these factors have on the $D(E_F)$ value and, therefore, on the critical temperature. However, it is necessary to consider that the peak positions on the $T_c(x)$ dependence in both investigated sample series correspond to the calcium content range in which the Fermi level pinning effect is observed. Therefore, it is possible to suppose that this is the $D(E_F)$ variation under calcium doping that results in the observed complicated $T_c(x)$ dependences in the $Y_{0.75-x}Ca_xPr_{0.25}Ba_2Cu_3O_y$ system.

Conclusions

This paper presents the experimental study results on the thermopower in two series of $Y_{0.75-x}Ca_xPr_{0.25}Ba_2Cu_3O_y$ samples with different oxygen subsystem conditions and their quantitative analysis using the narrow-band model. The obtained results and conclusions can be summarised as follows.

1) The critical temperature in the $Y_{0.75-x}Ca_xPr_{0.25}Ba_2Cu_3O_y$ system changes insignificantly and non-monotonically as the calcium content increases and its maximum position depends on the oxygen subsystem condition in the corresponding sample series.
2) Contrary to other calcium-containing systems, increased calcium content in the $Y_{0.75-x}Ca_xPr_{0.25}Ba_2Cu_3O_y$ system does not lead to a rise in the $S(T)$ slope and leads to a narrowing of the band responsible for the conduction process. Both these effects can be associated with praseodymium and calcium ions interaction that weakens hybridisation of the praseodymium and band states.
3) The Fermi level position variation in the $Y_{0.75-x}Ca_xPr_{0.25}Ba_2Cu_3O_y$ samples is related to its pinning inside the local calcium-induced peak in the density-of-states function formed as the calcium content increases.
4) Although several factors affect the value of the density-of-states function at the Fermi level in the $Y_{0.75-x}Ca_xPr_{0.25}Ba_2Cu_3O_y$ system, the observed variations in the critical temperature are determined by the $D(E_F)$ change under doping and can be explained by doping-induced modification of the normal-state energy spectrum under the Fermi level pinning effect.

References

Awana, V. P. S., Malik, S. K., Yelon, W. B. (1996) Structural aspects and superconductivity in oxygen-deficient $Y_{1-x}Ca_xBa_2Cu_3O_{7-y}$ ($y \approx 0.3$) systems A neutron-diffraction study. *Physica C: Superconductivity*, 262 (3-4), 272–278. DOI: 10.1016/0921-4534(96)00213-4 (In English)

Elizarova, M. V., Gasumyants, V. É. (1999) Superconductivity, Seebeck coefficient, and band structure transformation in $Y_{1-x}Ca_xBa_2Cu_{3-x}Co_xO_y$ ($x = 0–0.3$). *Physics of the Solid State*, 41 (8), 1248–1255. DOI: 10.1134/1.1130976 (In English)

Fisher, B., Genossar, J., Kuper, C. G. et al. (1993) Effects of substituting calcium for yttrium on the properties of $YBa_2Cu_3O_{7-\delta}$. *Physical Review B*, 47 (10), 6054–6059. DOI: 10.1103/PhysRevB.47.6054 (In English)

Gasumyants, V. E. (2001) Analysis of the electron transport phenomena in HTSC-materials as the method of studying the band spectrum and its transformation under doping by different impurities. In: F. Gerard (ed.). *Advances in condensed matter and materials research. Vol. 1.* New York: Nova Science Publ., pp. 135–200. (In English)

Gasumyants, V. E., Elizarova, M. V., Patrina, I. B. (2000) Thermoelectric power and band spectrum transformation in $Y_{1-x}Ca_xBa_{2-x}La_xCu_3O_y$. *Superconductor Science and Technology*, 13 (12), 1600–1606. DOI: 10.1088/0953-2048/13/12/306 (In English)

Gasumyants, V. E., Elizarova, M. V., Vladimirskaya, E. V., Patrina, I. B. (2000) Ca effect on the normal-state and superconducting properties of Y-based HTS. *Physica C: Superconductivity*, 341–348, pt 1, 585–588. DOI: 10.1016/S0921-4534(00)00604-3 (In English)

Gasumyants, V. E., Kaidanov, V. I., Vladimirskaya, E. V. (1995) The electron transport phenomena in Y-based HTSC's and their analysis on the basis of phenomenological narrow-band theory. The band structure transformation with oxygen content and substitution for Cu. *Physica C: Superconductivity*, 248 (3-4), 255–275. DOI: 10.1016/0921-4534(95)00173-5 (In English)

Gasumyants, V. E., Martynova, O. A. (2017) Chapter 4. Specific features of the thermopower behavior of calcium-containing Y-based high-temperature superconductors: Experimental investigation and interpretation. In: A. Reimer (ed.). *Horizons in world physics. Vol. 291.* New York: Nova Science Publ. pp. 129–216. (In English)

Gasumyants, V. É., Vladimirskaya, E. V., Elizarova, M. V., Ageev, N. V. (1998) The possibility of introducing additional states in the conduction band of $YBa_2Cu_3O_y$ by Ca doping. *Physics of the Solid State*, 40 (12), 1943–1949. DOI: 10.1134/1.1130710 (In English)

Gasumyants, V. E., Vladimirskaya, E. V. Patrina, I. B. (1997) Analysis of the possible reasons for the suppression of superconductivity in the $Y_{1-x}Pr_xBa_2Cu_3O_y$ system on the basis of thermoelectric power data. *Physics of the Solid State*, 39 (9), 1352–1357. DOI: 10.1134/1.1130077 (In English)

Gasumyants, V. E., Vladimirskaya, E. V., Patrina, I. B. (1994) Transport properties, band spectrum, and superconductivity in the $Y_{1-x}Ca_xBa_2Cu_{3-z}Co_zO_y$ system. *Physica C: Superconductivity*, 235–240, pt 2, 1467–1468. DOI: 10.1016/0921-4534(94)91958-5 (In English)

Ghorbani, S. R., Andersson, M., Rapp, Ö. (2003) Normal state Hall effect in $Nd_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$: Competition between added charge and disorder. *Physica C: Superconductivity*, 390 (2), 160–166. DOI: 10.1016/S0921-4534(03)00700-7 (In English)

Iye, Y. (1992) Transport properties of high T_c cuprates. In: D. M. Ginsberg (ed.). *Physical properties of high temperature superconductors III.* Singapore: World Scientific Publ., pp. 285–361. DOI: 10.1142/9789814439688_0004 (In English)

Jirák, Z., Hejtmánek, J., Pollert, E. et al. (1988) Structure and superconductivity in $Y_{1-x}Ca_xBa_2Cu_3O_7$. *Physica C: Superconductivity*, 156 (5), 750–754. DOI: 10.1016/0921-4534(88)90153-0 (In English)

Kaiser, A. B., Ucher, C. (1991) Thermoelectrisity of high-temperature superconductors. In: A. V. Narlikar (ed.). *Studies of high temperature: Superconductors advances in research and applications. Vol. 7.* New York: Nova Science Publ., pp. 353–392. (In English)

Komarova, O. S., Gasumyants, V. E. (2010) Determination of the parameters of the normal state in doped yttrium high-temperature superconductors from thermopower coefficients in terms of different models of electron transport. *Physics of the Solid State*, 52 (4), 671–679. DOI: 10.1134/S1063783410040013 (In English)

Komarova, O. S., Martynova, O. A., Gasumyants, V. E. (2013) Doping-induced variations of the Fermi level in calcium-containing Y-based HTSC and their influence on the critical temperature. *Physica C: Superconductivity*, 495, 19–24. DOI: 10.1016/j.physc.2013.07.010 (In English)

Liu, R. S., Cooper, J. R., Loram, J. W. et al. (1990) Induced superconductivity in tetragonal $YBa_2Cu_3O_6$ by incorporation of Ca. *Solid State Communications*, 76 (5), 679–683. DOI: 10.1016/0038-1098(90)90115-R (In English)

Manthiram, A., Lee, S.-J., Goodenough, J. B. (1988) Influence of Ca on superconductivity of $Y_{1-x}Ca_xBa_2Cu_3\ O_{7-\delta}$. *Journal of Solid State Chemistry*, 73 (1), 278–282. DOI: 10.1016/0022-4596(88)90080-1 (In English)

Martynova, O. A., Gasumyants, V. É. (2006) Mechanism governing modification of the properties of the normal state and the critical temperatures under codoping of $YBa_2Cu_3O_y$ by calcium and praseodymium. *Physics of the Solid State*, 48 (7), 1223–1229. DOI: 10.1134/S106378340607002X (In English)

Martynova, O. A., Gasumyants, V. E., Babichev, A. V. (2011) Specific features of praseodymium-doping induced changes in the critical temperature and energy spectrum parameters of $YBa_2Cu_3O_y$ in the presence of calcium ions in the lattice. *Physics of the Solid State*, 53 (9), article 1769. DOI: 10.1134/S1063783411090198 (In English)

Martynova, O. A., Potapov, D. V., Gasumyants, V. E., Vladimirskaya, E. V. (2011) Mechanism of a strong rise of T_c due to the calcium doping in $Y_{1-x}Ca_xBa_2Cu_{2.8}Zn_{0.2}O_y$. *Physica C: Superconductivity*, 471 (9-10), 308–313. DOI: 10.1016/j.physc.2011.02.011 (In English)

McCarron III, E. M., Crawford, M. K., Parise, J. B. (1989) Observation of superconductivity in $(Y_{1-x}Ca_x)Ba_2Cu_3O_6$. *Journal of Solid State Chemistry*, 78 (1), 192–196. DOI: 10.1016/0022-4596(89)90145-X (In English)

Ong, N. P. (1990) The Hall effect and its relation to other transport phenomena in the normal state of the high-temperature superconductors. In: D. M. Ginsberg (ed.). *Physical properties of high temperature superconductors II.* Singapore: World Scientific Publ., pp. 459–508. (In English)

Parise, J. B., McCarron III, E. M. (1989) The structure of the 44 K superconductor $(Y_{1-x}Ca_x)Ba_2Cu_3O_{6+\delta}$ ($\delta \leq 0.2$). *Journal of Solid State Chemistry*, 83 (1), 188–197. DOI: 10.1016/0022-4596(89)90068-6 (In English)

Tokiwa, A., Syono, Y., Kikuchi, M. et al. (1988) Crystal structure and superconductivity controlled by cation substitution and oxygen annealing in $Y_{1-x}Ca_xBa_2Cu_3O_y$ and $YBa_{2-x}La_xCu_3O_y$. *Japanese Journal of Applied Physics*, 27 (6A), article L1009. DOI: 10.1143/JJAP.27.L1009 (In English)

Vladimirskaya, E. V., Gasumyants, V. E., Patrina, I. B. (1995) Influence of double substitutions on transport properties, superconductivity, and band spectrum in the $YBa_2Cu_3O_y$ system. *Physics of the Solid State*, 37 (7), 1084–1087. (In English)