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Superconducting and Electrotransport Properties of $Y_{0.89}R_{0.11}Ba_2Cu_3O_{7-\delta}$ (R=La, Pr) Polycrystals

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Abstract. The superconducting and electrotransport properties were studied in $Y_{0.89}R_{0.11}Ba_2Cu_3O_{7-\delta}$ polycrystals, with the same concentration of rare earth metal elements (R = La, Pr) but with different valence and magnetic moments, by recording the temperature dependence ρ(T) curves of the resistivity in the temperature range (77-300) K. It was considered the influence of La and Pr on the width of the superconducting transition of the samples (ΔT_C), its critical temperature (determined by the onset of transition - T_C^{on} and the offset - T_c^0), the absolute values of the resistivity of the fluctuation and normal regions ρ(300 K) and ρ(100 K)], as well as on their ratio [$\boldsymbol{a}$ = ρ(300 K)/ρ(100 K)]. It has been revealed that there is a certain correlation between the aforementioned characteristics. It is emphasized that Pr is more critical than La in terms of its effect on characteristics. It is believed that the different behavior of the correlations observed between these characteristics for La and Pr is largely due to the differences in their ionic radii, displayed valence, as well as their intrinsic magnetic moments. It is shown that these differences in the case of La and Pr are manifested in the form of the phase separation phenomenon and the "Pr- anomaly", respectively.

Keywords: high temperature superconductor, superconducting transition, superconducting transition width, onset and offset temperature, phase separation phenomenon

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1. Introduction

The mechanism of superconductivity actually operating in high-temperature superconductors (HTSCs) at the microscopic level has not been elucidated so far. It is an important fundamental problem both from the point of view of solid state physics and its application. The application of HTSCs is limited by their still low values of critical temperature (T_c) and current (J_c) [1, 2]. Therefore, the study of changes in the critical characteristics of $YBa_2Cu_3O_y$ (Y-123) systems under the influence of various factors is a topical issue, which will contribute to the discovery of the mechanism of superconductivity, as well as obtaining compounds with higher characteristics [2-5]. In order to change the critical characteristics of Y-123 superconductors, hydrostatic pressure or replacement of Y atoms with other rare earth elements (R) is applied ("internal" or "chemical pressure") [2-5]. It was found that the nature of the change in the critical and structural characteristics of the $Y_{1-x}R_xBa_2Cu_3O_y$ compound largely depends on the ionic radius of R, its concentration (x) and valence [1, 3, 4, 6-10]. Thus, among the R elements that replace Y, it is particularly important to study the effects of Pr and La in Y-123, because the first of them can appear in both trivalent and tetravalent states, and the second only in trivalent [1, 5, 10-12]. In addition, the ionic radius of La is larger than the ionic radii corresponding to the two valence states of Pr. It is also known that Pr, having a smaller ionic radius and higher valence than Ba^{2+}, can replace both Ba^{2+} and Y^{3+} in Y-123 [4, 5, 9]. Moreover, in the case of Ba^{2+} substitution, the decrease of Tc along with the increase in Pr concentration occurs much faster than if it is substituted for Y^{3+} [4, 5, 9]. It should also be noted that the Pr ion has its intrinsic large magnetic moment, while La does not, which in the case of Pr, unlike La, can significantly worsen the superconducting characteristics of Cooper pairs. [1,7,8,11,13]. However, some issues related to the effect of Pr and La on the electrotransport properties in the Y-123-system remain incompletely resolved. In particular, the question of the mechanism of effect on superconducting and normal properties ("Pr anomaly") caused by the introduction of Pr atoms still remains controversial [10,14-17].

The present work aims to investigate the effect of Pr and La on the superconducting and electrotransport properties of $Y_{0.89}R_{0.11}Ba_2Cu_3O_{7-\delta}$ compounds through temperature measurements of resistivity.

2. Experimental methods

Two samples of compositions $Y_{1-x}R_xBa_2Cu_3O_{7-\delta}$ were prepared for R=Pr,La with x = 0.11. The studied samples $Y_{0.89}Pr_{0.11}Ba_2Cu_3O_{7-\delta}$ (Y-Pr) and $Y_{0.89}La_{0.11}Ba_2Cu_3O_{7-\delta}$ (Y-La) were synthesized by the standard solid-phase technique [1]. The starting reactants were Y_2O_3, Pr_6O_{11}, La_2O_3, CuO and $BaCO_3$. The corresponding amounts of reagents were mixed thoroughly in an agate mortar, pelletized, and annealed at 930°C. The synthesis, including seven intermediate crushings and pressings, lasted 160 h. Long procedures favor ordering of R elements substitution in yttrium positions [1]. Once the synthesis was completed, the samples were annealed at a temperature of 300 °C for 3 h and cooled slowly in the furnace to room temperature to reach oxygen saturation. The temperature dependence of resistivity ρ(T) was measured by the standard four-probe technique with the bias current 10 mA in the temperature region (77 - 300) K [18, 19]. Samples have a rectangular cross section (1.8 mm × 1.7 mm), the distance between the potential contacts being 2 mm. The onset (T_c^{on}) and offset (T_c^0) of the superconducting transition was determined by the drop in the normal state resistivity (ρ_n) of the sample at 10 and 90%, respectively, and the width of the transition was $\Delta T_c = T_c^{on} - T_c^0$ [17]. In order to gain an additional insight of the electrotransport processes taking place in the samples, the values of resistivity ρ(300 K) and ρ(100 K), as well as their relationship [***a*** = ρ(300 K)/ρ(100 K)] were compared with the superconducting characteristics [14, 15]. Moreover, a larger value of both T_c and ***a*** may also indicate a more perfect structure of the studied sample [14-17].

3. Results and Discussions

Fig. 1 shows the curves of the temperature dependence of the resistivity ρ(T) of Y-La and Y-Pr samples in the temperature region (80 - 100) K. The table below shows the critical temperatures of the onset (T_c^{on}) and offset (T_c^0) of the superconducting transition of these samples, the transition widths (ΔT_c), the absolute values of the resistivity ρ(300 K) and ρ(100 K) as well as their ratio: ***a*** = ρ(300 K)/ρ(100 K). It can be seen from Fig. 1 that in both samples (Y-La and Y-Pr) in the range of temperatures $T > T_c^{on}$, the ρ(T) exhibits a metallic behavior: dρ/dT>0, i.e. ρ increases as the temperature increases. In those samples T_c^{on} is 90.5 K and 83.6 K, respectively, and T_c^0 is 86.5 K and 80.5 K (Fig. 1 and Table 1.). That is, the superconducting transition in the Y-Pr sample, compared to Y-La, is shifted to the lower temperature range by an average of 6.5 degrees, and ΔT_c in them is 3.1 K and 4 K, respectively. Note also that the resistivity of the Y-Pr sample in the range of temperatures below 88.5 K, starting from 85 K, exceeds that of Y-La by more than 2.5 orders of magnitude (Fig. 1). This ratio decreases rapidly with increasing temperature and the resistivity in both samples equalize at 88.5 K. As the temperature increases further, the opposite picture is observed, when the resistivity of the Y-La sample begins to noticeably increase compared to Y-Pr (Fig.1 and Table 1). Thus, at 100 K the resistivity in Y-La and Y-Pr samples is 2150 μΩ·cm and 1180 μΩ·cm, respectively, and at 300 K it is 2700 μΩ·cm and 1720 μΩ·cm. That is, the resistivity of the Y-La- sample compared to Y-Pr at 100 K is greater by 82%, and at 300 K by 57%. ***a*** is 1.26

and 1.46 for Y- La and Y-Pr samples, respectively. Moreover, ρ, T_c, ΔT_c characteristics and ***a*** in the samples are in the opposite correlation (Fig. 1 and Table 1).

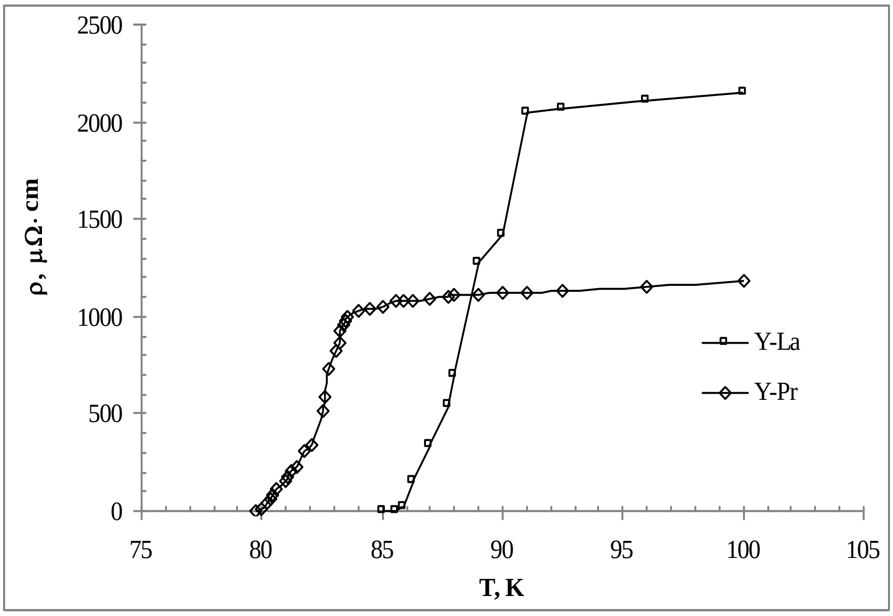

Fig. 1. ρ (T) dependence curves of Y-La and Y-Pr samples in the range (80-100) K.

Table 1 Some superconducting and electrotransport characteristic values of Y-La and Y-Pr samples.

sample	x	ρ(300 K), μΩ·cm	ρ(100 K), μΩ·cm	***a***=ρ(300 K)/ρ(100 K), A.U.	T_c^{on}, K	T_c^0, K	ΔT_c, K
Y-La	0.11	2700	2150	1.26	90.5	86.5	4
Y-Pr	0.11	1720	1180	1.46	83.6	80.5	3.1

That is, larger values of ρ, T_c, and ΔT_c correspond to smaller values of *a* and vice versa. The following facts should be considered when interpreting these results. Thus, the ionic radius of La is greater than that of Pr and the valency is 3, while Pr exhibits a mixed valence of 3 and 4. However, the tetravalent (Pr^{4+}) ion, compared to the trivalent (Pr^{3+}), has a smaller radius, which is very close to the radius of Y^{3+} and can easily substitute it [5, 7, 8, 12].

On the other hand, the Pr ion, unlike La, has its intrinsic magnetic moment, which can also lead to the deterioration of superconducting and electrotransport characteristics [8, 13, 16].The simultaneous effect of all these factors in the case of Y^{3+} placement can lead to the fact that Pr, unlike La, causes redistribution of charges in addition to tensile stresses in the elementary cell. It is worth emphasizing that in our case the sufficiently high value of T_c^{on} (90.5 K) observed in the Y-La sample is close to the temperatures observed for samples containing 1 to 10 % La by other authors [1, 3]. On the other hand, in the range of temperatures higher than 88.5 K, the sufficiently large value of the resistivity of Y-La compared to Y-Pr can probably be explained by the phase inhomogeneity of the first sample [3]. Indeed, in the compound $Y_{1-x}La_xBa_2Cu_3O_y$ [(Y–La)123] in the concentration range $0 \leq x \leq 1$, the phenomenon of so-called "phase separation" is stimulated and the Y-La main phase coexists with different amounts of superconducting La123 ($45\ K \leq T_c^{on} \leq 93\ K$), as well as with the non-superconducting phase $BaCuO_2$ [3]. This phenomenon may also be a possible reason for the relatively high resistivity observed in the (Y-La) sample. Note that according to [1], the Y-123 samples containing 11% La and Pr were sufficiently homogeneous, and their T_c^{on} was 92 K and 83.5 K, respectively, which are very close to our values (90.5 K and 83.6 K) (see Table 1). In the low-temperature (fluctuation) range, the resistivity behaviors obtained by us in both samples agree with the results obtained in [1], i.e. the resistivity of samples containing Pr is much higher than that of samples containing La. And the reason for this is that the introduction of even 5 % Pr leads to a strong localization of current carriers in the sample and a huge increase in its resistivity [10]. However, in our sample containing 11 % Pr, the resistivity in the normal state showed a lower value than that containing La, which contradicts the result observed in the above mentioned work [1]. Qualitatively similar results to our results were observed here for much smaller concentrations of Pr and La (x << 0.11), but the difference in resistivities was small and did not exceed (10-15) % [1]. It is worth noting that other researchers also confirmed that samples containing up to 10 % Pr had a more homogeneous structure compared to La [3, 20]. Our results indicate that the width of the superconducting transition in the Y-Pr sample (3.1 K) is smaller than that in the Y-La sample (4 K), which contradicts the results obtained in [1]. Moreover, the substitution for Y by Pr atoms in CuO_2 planes causes oxygen vacancies, which lead to noticeable deformation fields affecting superconductivity. These defects can become pinning centers for magnetic vortices penetrating into CuO_2 planes (grains) [1, 4]. And such a high value of T_c^{on} in the Y-La sample indicates that at a low concentration, the La^{3+} ion replaces Y^{3+}, which prefers it in size, and settles not inside the superconducting grains (in the CuO_2 planes), but on their edges (in CuO chains), causing mainly defects responsible for the reduction of T_c^0 - weakly bound oxygen vacancies. Note also that the larger value (1.46) observed for $\boldsymbol{a}$ in the Y-Pr-sample indicates a higher quality of the sample, which is characterized by a lower resistivity in the normal state and a sharper transition to the superconducting state, but with a significantly smaller T_c [14-17]. The values we obtained for $\boldsymbol{a}$ (1.26 and 1.46) are characteristic for rare earths and are close to the value observed for Ce, 1.43 [21].

In the range of high temperatures, T > 89 K, Y-La has a larger ρ compared to Y-Pr. However, in the low temperature range, ρ for Y-Pr, compared to Y-La, is incomparably large, the possible reason of which is the large magnetic moments of Pr ions [7, 13, 16]. The interaction of the superconducting pairs with these moments leads to a larger deformation of the spatial lattice and, therefore, a larger decrease in T_c, as well as a huge increase in ρ in contrast to Y-La. This is due to the fact that La^{3+} ions have no intrinsic magnetic moment [7], which leads to such a difference in the observed behavior of electrotransport characteristics. It should be noted that this difference in HTSC polycrystals, which is also expressed by the ratio $\boldsymbol{a} = \rho(300\,K)/\rho(100\,K)$, is not directly determined only by the resistivity of the intergranular environment, but also by resistivity of the grains [14-17, 22]. It turns out that partial substitution of Y by La with a larger ionic radius causes tensions in the spatial lattice, which stipulates a strong scattering of current carriers. This, in turn, leads to an increase in resistivity. In addition, La ions mostly accumulate at grain boundaries and are not pinning centers for magnetic vortices [1]. In this work, it is also shown that Pr ions penetrate into the interior of superconducting grains and become pinning centers for magnetic vortices, which in our case probably leads to a significant decrease in the normal state resistivity and transition width of the sample compared to the sample containing La.

The final identification of the reasons for the obtained results requires further new research.

4. Conclusions

The superconducting and electrotransport properties of $Y_{0.89}Pr_{0.11}Ba_2Cu_3O_{7-\delta}$ (Y-Pr) and $Y_{0.89}La_{0.11}Ba_2Cu_3O_{7-\delta}$ (Y-La) polycrystalline compounds were studied by recording the temperature dependence ρ(T) curves of resistivity in the temperature (77-300) K range. The following main results were obtained. The superconducting transition in the (Y-Pr) sample (3.1 K) is narrower than that in (Y-La) (4 K) and is shifted to the lower temperature range by about 6.5 K. Both compounds exhibit metallic behavior, but the resistivity of the sample (Y-Pr) in the fluctuation range is at least 2.5 orders of magnitude greater than that of (Y-La). However, at 100 K and 300 K, the opposite picture is observed, when the resistivity of the (Y-Pr) sample relative to (Y-La) decreases by 82 %

and 57 %, respectively. The superconducting and electrotransport properties observed in (Y-La) and (Y-Pr) samples are believed to be due to differences in the valences and magnetic moments of both the La and Pr ions.

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