PHYSICAL REVIEW B VOLUME 61, NUMBER 18 1 MAY 2000-II

Effect of praseodymium on the normal-state and superconducting properties of $R\mathrm{Ba_2Cu_3O}_y$: A comparative study of the role of the Pr ion on R and Ba sites

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(Received 10 May 1999; revised manuscript received 13 October 1999)

We present results of a comparative study of the normal-state and superconducting properties in the $R\mathrm{Ba_2Cu_3O}_y$ system with substitutions by Pr for the R and Ba sites. The temperature dependences of the resistivity and thermopower were measured for the $\mathrm{SmBa}_{2-x}\mathrm{Pr}_x\mathrm{Cu_3O}_y$ ($x=0.0-0.35$) samples and analyzed in comparison with data for the $\mathrm{Y}_{1-x}\mathrm{Pr}_x\mathrm{Ba_2Cu_3O}_y$ system. It was observed that the Pr→Ba substitution affects all the properties of the $R\mathrm{Ba_2Cu_3O}_y$ system, both the normal state and superconducting, much stronger compared to the Pr→Y one. This manifests itself in an increasing oxygen content, an orthorhombic-to-tetragonal transition at $x=0.3-0.35$, a stronger rise of the thermopower value, and a faster T_c drop. The results obtained are analyzed within a phenomenological narrow-band model in order to reveal both common peculiarities and specific features of the Pr influence on the band spectrum parameters in the normal state when substituting for different lattice positions. We have observed that the Pr doping leads to a significant modification of the band spectrum, resulting in a strong band broadening and states localization. At the same time, changes of the total effective width of the conduction band W_D and the T_c value in two systems with the different kind of Pr doping are shown to correspond to each other so that the $T_c(W_D)$ dependence follows the universal correlation for the $\mathrm{YBa_2Cu_3O}_y$ system with different deviations from stoichiometry. Based on our analysis and in agreement with earlier suggestions, we conclude that the superconductivity suppression in both Pr-doped systems could be mainly attributed to the hybridization between $4f$ states of the Pr ion and the conduction-band states. In addition, Pr in $\mathrm{SmBa}_{2-x}\mathrm{Pr}_x\mathrm{Cu_3O}_y$ on the Ba site acts like other trivalent rare-earth impurities inducing the extra hole filling effect that leads to a stronger T_c suppression compared to $\mathrm{Y}_{1-x}\mathrm{Pr}_x\mathrm{Ba_2Cu_3O}_y$.

I. INTRODUCTION

Among different elements substituting for the native cations in the $\mathrm{YBa_2Cu_3O}_y$-type high-T_c superconductors (HTSC's) Pr has attracted much attention (for a general review, see Ref. 1). It was widely reported that despite the fact that $\mathrm{PrBa_2Cu_3O}_y$ is orthorhombic and isostructural to $R\mathrm{Ba_2Cu_3O}_y$ (R is Y or a rare-earth element except Ce and Tb), the former compound does not exhibit superconductivity.[2–4] With increasing Pr doping in $\mathrm{Y}_{1-x}\mathrm{Pr}_x\mathrm{Ba_2Cu_3O}_y$ the critical temperature decreases and goes to zero at $x_c=0.55$.[2,5]

Numerous studies have been performed to investigate both the normal-state and superconducting properties of the $\mathrm{Y}_{1-x}\mathrm{Pr}_x\mathrm{Ba_2Cu_3O}_y$ system and to elucidate the mechanism responsible for the suppression of superconductivity. Several possible models have been earlier proposed, such as (i) the hole filling effect arising from the valence of the Pr ion which could be much greater than 3+,[4,6,7] (ii) the pair-breaking model suggesting that superconductivity is destroyed due to the interaction of the Pr magnetic moments and the spin of the mobile holes,[8–10] (iii) the effect of the hybridization between $4f$ states of the Pr ion and the conduction-band states which leads to the localization of the charge carriers or to significant changes in the band structure.[11–15] In most of recent papers it is argued that the T_c suppression is mainly caused by the hybridization effect[16–20] or, at least, by a coexistence of the pair-breaking and hybridization effects.[21] A recent short review presenting the arguments in favor of the hybridization model can be found in Ref. 22.

We have previously performed an analysis of the normal-state transport properties for the $\mathrm{Y}_{1-x}\mathrm{Pr}_x\mathrm{Ba_2Cu_3O}_y$ system within a narrow-band model.[23] This model was shown to allow one to estimate the main band spectrum parameters, to trace their transformation with increasing doping level in the $\mathrm{YBa_2Cu_3O}_y$ system, and to compare the modification of the conduction band with varying superconducting properties.[24–27] Applying this model to the Pr-doped samples we have come to the conclusion that the main reason for the superconductivity suppression is rather to be a strong modification of the conduction band caused by praseodymium.[23]

It was recently reported by several groups about successful preparation of single-phase $R\mathrm{Ba}_{2-x}\mathrm{Pr}_x\mathrm{Cu_3O}_y$ samples where Pr substitutes for the Ba site.[28–32] In this case Pr obviously being a nonisovalent impurity is expected to decrease the mobile hole concentration. There are two main questions to be answered: (i) whether or not the Pr ion on the Ba site affects the normal-state and superconducting properties of the $R\mathrm{Ba}_{2-x}\mathrm{Pr}_x\mathrm{Cu_3O}_y$ system like other trivalent rare-earth ions (for example, La), and (ii) whether or not the hybridization effect is realized when Pr substitutes for Ba. For this reason a comparative study of the $R_{1-x}\mathrm{Pr}_x\mathrm{Ba_2Cu_3O}_y$ and $R\mathrm{Ba}_{2-x}\mathrm{Pr}_x\mathrm{Cu_3O}_y$ system is of considerable interest due

TABLE I. Lattice parameters and oxygen content in $SmBa_{2-x}Pr_xCu_3O_y$ samples.

x	y	a, Å	b, Å	c, Å
0.0	6.94	3.847	3.902	11.735
0.1	6.99	3.853	3.900	11.700
0.15	7.02	3.850	3.898	11.690
0.2	7.04	3.862	3.888	11.665
0.3	7.07	3.878	3.883	11.630
0.35	7.10	3.875	3.875	11.625

to a possibility to investigate the Pr effect when it acts as either an isovalent or a nonisovalent impurity. At present, the question on different and common features of the Pr→R and Pr→Ba substitutions undoubtedly calls for further investigations because of a lack of experimental results on the Pr substitution for the Ba site.

The purpose of the present work is to perform a comparative analysis of the normal-state resistivity and thermopower as well as of the superconducting properties of the $Y_{1-x}Pr_xBa_2Cu_3O_y$ and $SmBa_{2-x}Pr_xCu_3O_y$ systems. The results obtained for the last system will be interpreted in the framework of a narrow-band model. Using this approach, we will analyze the band spectrum transformation and the variation of the critical temperature in the case of Pr→Ba doping in comparison with those obtained earlier for the $Y_{1-x}Pr_xBa_2Cu_3O_y$ system.[23] Based on these results we will discuss the role of Pr ions on different sites in the $RBa_2Cu_3O_y$ lattice as well as both common peculiarities and specific features of the superconductivity suppression by Pr when substituting for the R and Ba sites.

II. SAMPLES AND EXPERIMENTAL DETAILS

We have investigated the normal-state transport properties of $SmBa_{2-x}Pr_xCu_3O_y$ ($x=0.0$–0.35) ceramic samples. The samples were prepared by the standard solid-state processing technique from the high-purity respective carbonates and oxides mixed in required proportions. The mixtures were heated at $T=950\,^{\circ}C$ for 24 h, reground, pressed into pellets and then sintered two or three times at $T=950$–$970\,^{\circ}C$ for 24 h with intermediate regrinding. Finally, the products were annealed in flowing oxygen at $T=450\,^{\circ}C$ for 24 h and slowly furnace cooled down to room temperature.

X-ray-diffraction analysis was used to characterize the samples' purity and to determine the lattice parameters. The oxygen content was determined by the iodometric titration technique with an accuracy of ± 0.01–0.02. All the samples were of single phase with the foreign impurity level less than 1–2%. The oxygen content and the lattice parameters as a function of doping are presented in Table I. Comparing these results with the data for $Y_{1-x}Pr_xBa_2Cu_3O_y$, one can see that substitutions by Pr for the Y and Ba sites influence all these parameters in a different way. In the case of Pr on the Y site the oxygen content is almost constant with doping level and the orthorhombic symmetry retains for all the samples up to $x=0.6$.[8,23,33,34] Contrary to this, in the case of Pr on the Ba site the oxygen content increases gradually with x and an orthorhombic-to-tetragonal transition was observed at $x=0.30$–0.35. Note that analogous lattice transformation and oxygen content change were observed in the $NdBa_{2-x}Pr_xCu_3O_y$ system.[28,29,31] The revealed difference in the Pr effect on structural properties of the $RBa_2Cu_3O_y$ system can be considered as an additional evidence that in the $SmBa_{2-x}Pr_xCu_3O_y$ system praseodymium indeed substitutes for Ba. In this connection it is necessary to note that substitutions for Ba by trivalent rare-earth elements, for instance, by either La or Eu,[26,35–39] lead to the same lattice transformation and oxygen content change. Thus Pr on the Ba site seems to influence the sample structure like other trivalent ions.

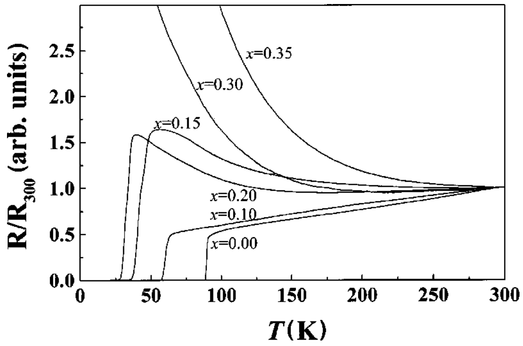

FIG. 1. Temperature dependences of the normalized resistivity for $SmBa_{2-x}Pr_xCu_3O_y$ samples.

The resistivity and thermopower were measured in the temperature range of $T=T_c-300$ K. The resistivity measurements were performed by the standard four-probe low-frequency ac (20 Hz) method. The thermopower was measured relative to copper electrodes and then 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.

III. EXPERIMENTAL RESULTS

The temperature dependences of the normalized resistivity for $SmBa_{2-x}Pr_xCu_3O_y$ are shown in Fig. 1. Peculiarities of the $\rho(T)$ dependence including its transformation with deviations from stoichiometry are typical for the HTSC materials. For the undoped sample the $\rho(T)$ curve is metalliclike, while for heavily doped samples the resistivity at low temperature demonstrates a semiconductorlike behavior. Note, that the Pr influence on the $\rho(T)$ transformation in the case of substitution for the Ba site is stronger compared to that for the Y site so that the metallic-semiconductor transition takes place at $x\approx 0.15$ for the $SmBa_{2-x}Pr_xCu_3O_y$ system and at $x\approx 0.4$ for the $Y_{1-x}Pr_xBa_2Cu_3O_y$ one.[23] The critical temperature T_c was determined as the midpoint of the resistive superconducting transition. The T_c variation with doping level for the $SmBa_{2-x}Pr_xCu_3O_y$ system in comparison with that for the $Y_{1-x}Pr_xBa_2Cu_3O_y$ one (taken from Ref. 23) is shown in Fig. 2. In the case of the Pr→Y substitution T_c decreases slightly in the range of $x=0.0$–0.1, goes down faster as the doping level increases further, and the superconductivity vanishes at the Pr content of $x=0.5$–0.6. The Pr→Ba substitution affects the superconducting properties much stronger and, as a result, the $SmBa_{2-x}Pr_xCu_3O_y$ system becomes nonsuperconducting at the Pr content of $x\approx 0.3$. To compare the influence of the Pr ion placed at dif-

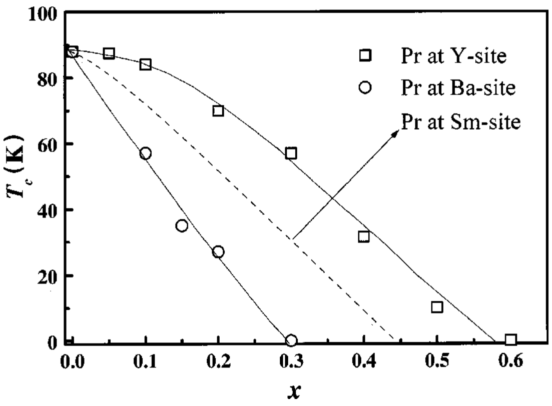

FIG. 2. Variation of the critical temperature with Pr content in $SmBa_{2-x}Pr_xCu_3O_y$ and $Y_{1-x}Pr_xBa_2Cu_3O_y$ (taken from Ref. 23). The $T_c(x)$ dependence for $Sm_{1-x}Pr_xBa_2Cu_3O_y$ samples according to the data in Refs. 18, 40, and 43 is shown by dashed line.

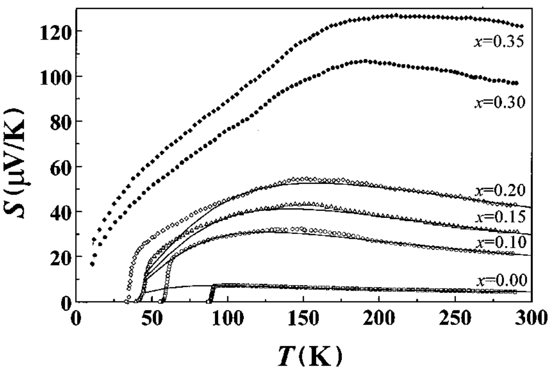

FIG. 3. Temperature dependences of the thermopower for $SmBa_{2-x}Pr_xCu_3O_y$ samples. Different symbols present the experimental data, solid lines are the best-fitted curves calculated by the model used.

ferent sites of the lattice, it is necessary to take into account the data on the rare-earth R ion-size effect on T_c in the $R_{1-x}Pr_xBa_2Cu_3O_y$ system. It was well-established that T_c at a given Pr content and a critical Pr content corresponding to the superconductivity disappearance in $R_{1-x}Pr_xBa_2Cu_3O_y$ decrease almost linearly with increasing radius of the R ion.[18,20,40–43] To explain this finding, authors of Refs. 18, 20, and 41 suggest that the hybridization between $4f$ states of the Pr ion and the conduction-band states enhances as the R ion radius increases that results in a stronger superconductivity suppression. Since the Sm ion radius is larger then the Y one, the T_c value even in the $Sm_{1-x}Pr_xBa_2Cu_3O_y$ system should drop faster compared to the $Y_{1-x}Pr_xBa_2Cu_3O_y$ one. Using the data mentioned above we have plotted in Fig. 2 the $T_c(x)$ dependence for the $Sm_{1-x}Pr_xBa_2Cu_3O_y$ system together with our data. It can be seen that the observed drop of T_c in $SmBa_{2-x}Pr_xCu_3O_y$ is even faster than it should be in case of Pr→Sm substitution. This fact clearly indicates that in the case of Pr→Ba substitution Pr has a twofold effect on T_c. In addition to the hybridization of $4f$ Pr states with band states praseodymium acts as an nonisovalent impurity and, as a result of two of these mechanisms, T_c in the $Sm_{1-x}Pr_xBa_2Cu_3O_y$ system falls much faster. Note that this conclusion is in a good agreement with results of Colonescu *et al.*[28] They have found that in the case of the insulating $Nd_{0.7}Pr_{0.3}Ba_2Cu_3O_y$ sample (where superconductivity is suppressed by the hybridization) substitution by Ca for Nd fails to restore superconductivity, whereas in the $NdBa_{1.7}Pr_{0.3}Cu_3O_y$ compound (which is also an insulator, but, in addition, due to the hole-filling effect) the same substitution raises the T_c value from zero to 31 K. These results have nicely shown that the suppression of superconductivity when the Pr ion occupies the Ba site may not result solely from the hybridization effect.

The temperature dependences of the thermopower are shown in Fig. 3. They demonstrate the well-known characteristic features of the thermopower behavior in the doped $RBa_2Cu_3O_y$ system (Ref. 44) being qualitatively analogous, in their main peculiarities, to those for the $Y_{1-x}Pr_xBa_2Cu_3O_y$ system.[23] For slightly doped samples the thermopower is almost temperature independent at $T > 150–200$ K depending on sample composition. With increasing doping level the $S(T)$ dependence at high temperatures becomes stronger. Besides, all the $S(T)$ curves show a well-pronounced maximum at a temperature above the superconducting transition which shifts towards higher temperatures with increasing doping level. On the other hand, the incorporation of praseodymium into the Y or Ba sites affects the thermopower to a different extent. To demonstrate this, the variation of the thermopower value at $T = 300$ K, S_{300}, with the Pr content for the $Sm_{1-x}Pr_xBa_2Cu_3O_y$ and $Y_{1-x}Pr_xBa_2Cu_3O_y$ systems is shown in Fig. 4. With increasing Pr content the S_{300} value increases slightly in $Y_{1-x}Pr_xBa_2Cu_3O_y$, but rises extremely strongly in $SmBa_{2-x}Pr_xCu_3O_y$ compared to other substitutions in the $RBa_2Cu_3O_y$ system reaching the value of about 120 μV/K at $x = 0.35$. In fact, this result can be considered as the direct evidence for the hole filling effect in the $SmBa_{2-x}Pr_xCu_3O_y$ system realized due to a higher valence of Pr compared to that of Ba. Thus the difference between the S_{300} variation for cases of different kinds of Pr doping is caused by different relation between the valences of Pr and substituted elements.

Before analyzing the results obtained, we would like to mention one more experimental fact. Comparing the $S(T)$ dependence for the $Y_{1-x}Pr_xBa_2Cu_3O_y$ (see Ref. 23) and $SmBa_{2-x}Pr_xCu_3O_y$ (see Fig. 3) systems, one can observe that the S_{300} values for the sample with $x = 0.4$ for the first case and $x = 0.1$ for the second one as well as for $x = 0.6$ and

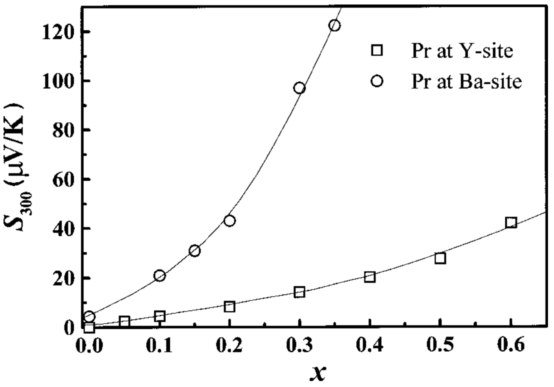

FIG. 4. Thermopower at $T = 300$ K as a function of Pr content in $SmBa_{2-x}Pr_xCu_3O_y$ in comparison with the data for $Y_{1-x}Pr_xBa_2Cu_3O_y$ (Ref. 23).

$x=0.2$, respectively, are equal. Moreover, even the $S(T)$ dependences for those couples of samples are very close to each other excluding a temperature region in the vicinity of the superconducting transition. But in both cases the T_c value for $Y_{1-x}Pr_xBa_2Cu_3O_y$ sample is less then for $SmBa_{2-x}Pr_xCu_3O_y$ (31.5 K for $x=0.4$ and 57 K for $x=0.1$ for the first couple of samples and <4 K for $x=0.6$ and 27 K for $x=0.2$ for the second one). This fact will be discussed below.

Summarizing the experimental results, we have observed that the Pr→Ba substitution affects all the properties of the $RBa_2Cu_3O_y$ system, both the normal-state and superconducting, much stronger compared to the Pr→Y one. Below we will analyze the normal-state transport properties on the basis of our phenomenological band spectrum model and compare the results obtained here on $SmBa_{2-x}Pr_xCu_3O_y$ with those for $Y_{1-x}Pr_xBa_2Cu_3O_y$.[23]

IV. DISCUSSION

To obtain the information on the conduction-band transformation in $SmBa_{2-x}Pr_xCu_3O_y$, we have used a narrow-band model described in detail in Ref. 24. Note, that various models have been proposed in order to describe the thermopower behavior in HTSC materials. Different authors have considered both single-[45–48] and two-band pictures,[49–52] analyzed the thermopower taking into account the presence of the van Hove singularity near the Fermi level,[53] the phonon drag effect,[54,55] and a bosonic contribution to the $S(T)$ dependences.[56,57] The question on validity of these models is still under discussion. It was demonstrated by different groups that several models, including the model we use, can reasonably fit the experimental $S(T)$ curves for both Y- and Bi-based HTSC's.[58–64] However, some of those models contain parameters having no clear physical interpretation. Besides, when applying those models to doped HTSC's, the parameters show, in some cases, no systematic variation or the values of them for some sample compositions look to be rather unphysical.[58,60–63] In our opinion, the advantages of our approach are (i) the use of only three parameters, each of them having a clear physical meaning characterizing the properties of the charge carrier system, and (ii) the possibility to describe simultaneously the resistivity, thermopower, and Hall coefficient behavior in the normal state of HTSC's for samples of different compositions. This allows us to reveal the conduction-band transformation under doping by different impurities and, comparing it with the T_c variation, to analyze the dopant effect on parameters of the charge carrier system in the normal state and superconducting properties of doped HTSC's.

Our model is founded on the assumption that a sharp peak in the density-of-states (DOS) function exists in the band spectrum of HTSC materials. It can be either a single narrow band or a sharp DOS peak on a wide band background appearing, for example, due to the van Hove singularity. In both cases, if the Fermi level is located in the region of this peak, it is its narrowness that mainly determines specific features of the electron transport phenomena in the normal state. This makes it possible to calculate the transport properties using the simplest rectangular approximation for the DOS and the differential conductivity functions.[24] In doing so, one can obtain the analytical expressions for the transport coefficients (for details, see Ref. 24) which contain three model parameters. These are the band filling F, which is equal to the ratio of the number of electrons to the total number of states in the band, the total effective bandwidth W_D, and the effective width of an energy interval of the electrons responsible for the conduction process W_σ.

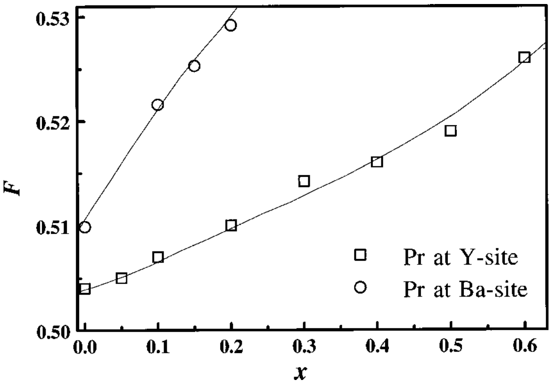

FIG. 5. Band filling F vs Pr content in $SmBa_{2-x}Pr_xCu_3O_y$ in comparison with the data for $Y_{1-x}Pr_xBa_2Cu_3O_y$ (Ref. 23).

Using this approach, we were able to achieve a good agreement between the experimental and calculated $S(T)$ dependences both for the $YBa_2Cu_3O_y$ system with various substitutions for the native cations[24–27,38] and Bi-based HTSC's.[65] This has permitted us to determine the band spectrum parameters for the investigated sample compositions, to analyze their variation depending on the type and content of different impurities, and to draw conclusions on reasons for the conduction-band transformation under doping.

Below we use the narrow-band model to analyze the thermopower in the $SmBa_{2-x}Pr_xCu_3O_y$ system. Note that the experimental data for samples with Pr content of $x=0.30$ and $x=0.35$ have been used only for qualitative analysis. Our calculations showed that for those compositions the conduction band becomes too wide (the W_D value is more then 600 meV). In such a case our model becomes far too rough and may give a wrong result. For $x<0.3$ we have obtained a reasonable agreement between the experimental results and calculated curves. To illustrate this, the best-fitted $S(T)$ curves are shown in Fig. 3. As one can see, the fits look to be reasonable excluding the region of low temperatures for heavily doped samples. This discrepancy is due to the same reason as it was noted above because the lower temperature is the worse the condition of the band narrowness is obeyed. It is necessary to note that in the framework of our model different fitting parameters affect different peculiarities of the $S(T)$ dependences that make it possible to determine the values of all the three parameters quite unambiguously.

The concentration dependence of the band filling for the $SmBa_{2-x}Pr_xCu_3O_y$ system in comparison with that for the $Y_{1-x}Pr_xBa_2Cu_3O_y$ one is shown in Fig. 5. It can be seen that the F value increases in both cases, but to a different extent. In our previous study[23] we have clearly shown that praseodymium, when substituting for Y, affects the band filling very insignificantly compared to a nonisovalent impurity. Taking into account the insignificant rise of the F value, unchanged oxygen number y, and a slight variation of the lattice parameters with doping level we have concluded that the valence of Pr is very close to 3+.[23] This conclusion is in a good

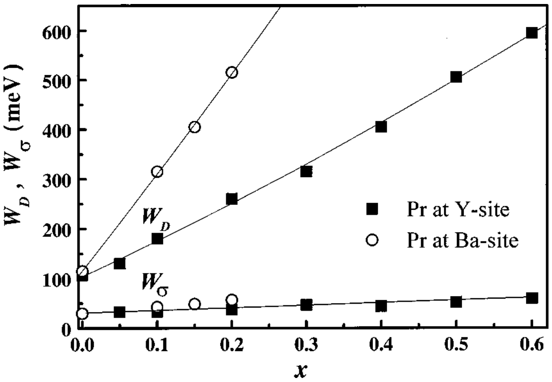

FIG. 6. Effective bandwidth W_D and conductivity bandwidth W_σ vs Pr content in $SmBa_{2-x}Pr_xCu_3O_y$ in comparison with the data for $Y_{1-x}Pr_xBa_2Cu_3O_y$ (Ref. 23).

agreement with the results of other authors[16,17] who proposed that in the $Y_{1-x}Pr_xBa_2Cu_3O_y$ system, though Pr is predominantly trivalent, an admixture of Pr^{4+} of about 10% exists.

Figure 5 shows that the F value in the case of the $SmBa_{2-x}Pr_xCu_3O_y$ system increases with doping level much stronger than in the $Y_{1-x}Pr_xBa_2Cu_3O_y$ one, and, at the same time, the $F(x)$ dependence is close to that for the $YBa_{2-x}La_xCu_3O_y$ system.[26] Thus both the structural changes (increasing oxygen content, an orthorhombic-to-tetragonal transition) and the band filling variations in the $SmBa_{2-x}Pr_xCu_3O_y$ and $YBa_{2-x}La_xCu_3O_y$ systems are analogous to each other. These facts make it possible to conclude that Pr on the Ba site has a valence of 3+ and acts like other nonisovalent rare-earth impurities.

The concentration dependences of the total effective bandwidth W_D and the ''conductivity'' effective bandwidth W_σ for Pr-doped samples are shown in Fig. 6. Before analyzing them, let us note that according to our previous results the variation of the W_σ/W_D ratio with changing sample composition characterizes the variation of the degree of the charge carriers localization in the band.[24] It can be seen that an increase in Pr content leads to an essential broadening of the conduction band in both $Y_{1-x}Pr_xBa_2Cu_3O_y$ and $SmBa_{2-x}Pr_xCu_3O_y$ accompanied by a gradual and strong rise of the localization degree (the decrease of the W_σ/W_D ratio). In the latter system the band broadening is extremely strong compared to other substitutions in $YBa_2Cu_3O_y$[24,26,38] and, as a result, even for the sample with $x=0.2$ W_D reaches the value of about 500 meV. To interpret these data, it is necessary to mention that in the framework of our model the reason for such a modification of the band spectrum is assumed to be the Anderson localization of the states[66] caused by a lattice disordering induced by substitutions for the native cations. As it was shown in Refs. 24, 26, and 38 in cases of different nonisovalent substitutions or an increasing oxygen deficit, the main reason for the band broadening and the localization of the states is a redistribution of oxygen atoms induced by an impurity and resulting in an oxygen subsystem disordering. Such a disordering does not occur, however, in the case of the $Y_{1-x}Pr_xBa_2Cu_3O_y$ system because the Pr→Y substitution has practically no effect on the oxygen content and the oxygen subsystem as a whole.[23] This fact allowed us earlier to conclude that the modification of the conduction band in the $Y_{1-x}Pr_xBa_2Cu_3O_y$ system is caused by the direct impact of the Pr impurity.[23] These results give support to the conclusion that the reason for the band spectrum modification with Pr doping is the hybridization between $4f$ states of the Pr ion and the conduction-band states accompanied by a strong localization of the states.[16,18–20,22,67]

Further, as one can see in Fig. 6, the bandwidth and the degree of the states localization rise with increasing doping in the $SmBa_{2-x}Pr_xCu_3O_y$ system much faster compared to the $Y_{1-x}Pr_xBa_2Cu_3O_y$ one. This is a result of a simultaneous effect of two mechanisms. First, as noted above Pr on the Ba site acts as a trivalent rare-earth impurity. If so, this should cause, in agreement with our previous results, both the band broadening and states localization. The incorporation of the Pr ions into the Ba sites induces a disordering of the oxygen subsystem that can be confirmed by an increasing oxygen content and a transition to the tetragonal symmetry (see Table I). However, comparing our results on the $La^{3+}\rightarrow Ba^{2+}$ substitution[26] with the case of the Pr→Ba one we can conclude that Pr has more essential effect upon the degree of the states localization and the effective bandwidth than the trivalent La ion has. For example, in the $YBa_{2-x}La_xCu_3O_y$ system in the range of $x=0.0-0.2$ a broadening of the band is less than 50 meV and the W_σ/W_D ratio changes by a factor of 1.5, while the W_D variation in the $SmBa_{2-x}Pr_xCu_3O_y$ system in the same impurity range is about 400 meV and the W_σ/W_D ratio changes by about 2.5 times. Consequently, one can conclude that on the background of the oxygen subsystem disordering induced by the Ba-site Pr effect, the hybridization of Pr $4f$ states with conduction-band states in the $SmBa_{2-x}Pr_xCu_3O_y$ system also takes place, like in the $Y_{1-x}Pr_xBa_2Cu_3O_y$ one. Moreover, as it was shown in Ref. 18 this hybridization is stronger in the $SmBa_{2-x}Pr_xCu_3O_y$ system compared to the $YBa_{2-x}Pr_xCu_3O_y$ one because of the difference between the Sm and Y ionic radii. Thus, due to the combination of two of those types of the Pr influence, the localization of the mobile holes in the case of the $SmBa_{2-x}Pr_xCu_3O_y$ system should be much stronger than in the $Y_{1-x}Pr_xBa_2Cu_3O_y$ one. Our results give a strong support to this point of view. As one can see in Fig. 6, the W_σ/W_D ratio decreases with doping much faster in $SmBa_{2-x}Pr_xCu_3O_y$ implying a more essential increase in the localization degree. In this connection, we would like to note that the stronger localization of the states in the $SmBa_{2-x}Pr_xCu_3O_y$ system compared to the $Y_{1-x}Pr_xBa_2Cu_3O_y$ one revealed by our analysis of the $S(T)$ dependences correlates well with the stronger $\rho(T)$ transformation [for example, as noted above, a transition to a semiconductorlike $\rho(T)$ behavior at low temperatures in $SmBa_{2-x}Pr_xCu_3O_y$ takes place at lower Pr content].

By such a way, an increase in the Pr content in the $SmBa_{2-x}Pr_xCu_3O_y$ system results in a very strong band spectrum modification, namely, the conduction-band broadening and the localization of the states at the edges of the band. In this connection let us discuss the transformation of the $S(T)$ dependences in the $SmBa_{2-x}Pr_xCu_3O_y$ and $Y_{1-x}Pr_xBa_2Cu_3O_y$ systems. As shown in Ref. 23 and noted above, the charge-carrier concentration in the $Y_{1-x}Pr_xBa_2Cu_3O_y$ system (or, in other words, the band filling in our model) depends slightly on the Pr content. In this case rising the slope of the $S(T)$ curves in the range of $T \approx 150-300$ K accompanied by increasing S_{300} is caused, in the framework of our model, by a gradual increase of the state's localization degree (the decrease of the W_σ/W_D ratio).[24] At the same time, a donorlike character of the $Pr^{3+}\rightarrow Ba^{2+}$ substitution results in the essential rise of the S_{300} value with doping level in the $SmBa_{2-x}Pr_xCu_3O_y$ system, on whose background the influence of a strong states localization on the $S(T)$ curves shape becomes less pronounced. Taking into account these different reasons for the $S(T)$ transformation in the investigated systems, one can explain the noted above fact that for the samples of the $SmBa_{2-x}Pr_xCu_3O_y$ and $Y_{1-x}Pr_xBa_2Cu_3O_y$ systems with the same S_{300} value T_c is higher in the first case. Indeed, it is obvious that the hybridization effect resulting in the strong band broadening should affect the T_c value stronger compared to the hole filling effect. On the other hand, the hole filling effect leads to a stronger S_{300} rise. As a result, the same S_{300} value is reached by the Pr→Ba substitution at a lower Pr content than by the Pr→Y one (see Fig. 4). It is clear that T_c in the first case should be higher in agreement with our experimental results.

Finally, let us discuss the common reason for the superconductivity suppression in the $RBa_2Cu_3O_y$ system with different deviations from stoichiometry. The data presented in Figs. 2 and 6 show that a stronger band broadening in the $SmBa_{2-x}Pr_xCu_3O_y$ system is accompanied by a faster T_c drop. We would like to note, that analyzing the band spectrum transformation in the $YBa_2Cu_3O_y$ system with increasing oxygen deficit[24] as well as under different nonisovalent substitutions[24,26] including the codoped system[68] we have concluded that there is the universal correlation between the effective bandwidth and the critical temperature value. The existence of such a correlation can be easily understood qualitatively. It is clear that doping cannot lead (at least in most cases) to an increase of the total number of states in the band. If so, a broadening of the band has to be accompanied by decreasing value of the DOS function at the Fermi level. The latter can be considered as the major reason for the T_c decrease. Thus the modification of the band spectrum in the normal state influences the superconducting properties of the $RBa_2Cu_3O_y$ system. For this reason it was interesting to check the presence of the $T_c(W_D)$ correlation in the case of Pr-doped samples. Results of this checking are shown in Fig. 7 together with the data for other doped $YBa_2Cu_3O_y$ systems taken from our previous publications. As one can see the $T_c(W_D)$ dependence for the $Y_{1-x}Pr_xBa_2Cu_3O_y$ and $SmBa_{2-x}Pr_xCu_3O_y$ systems also follows the universal correlation.[68] Note, that this finding points again to a slighter effect of the hole filling on the superconducting properties of the $RBa_2Cu_3O_y$ system compared to the band broadening. On the other hand, this fact can be considered as an evidence for the conclusion that praseodymium affects the superconducting properties of the $RBa_2Cu_3O_y$ system due to its influence on the band spectrum modification, i.e., like other nonisovalent impurities. A specific role of the Pr impurity manifests itself in the fact that due to an effect of the states hybridization praseodymium affects the structure of the conduction band drastically, inducing the strong band broadening accompanied by the strong states localization. Let us note that in the case of $Y_{1-x}Pr_xBa_2Cu_3O_y$ substitution for Ba_2 by BaSr and heat treating the samples in argon prior to oxygenation was demonstrated to increase the critical Pr content x_c to 0.7,[69] which seems to rule out the pair-breaking mechanism as the main course of the T_c suppression and to support therefore our point of view, as well as the conclusion drawn in Ref. 22.

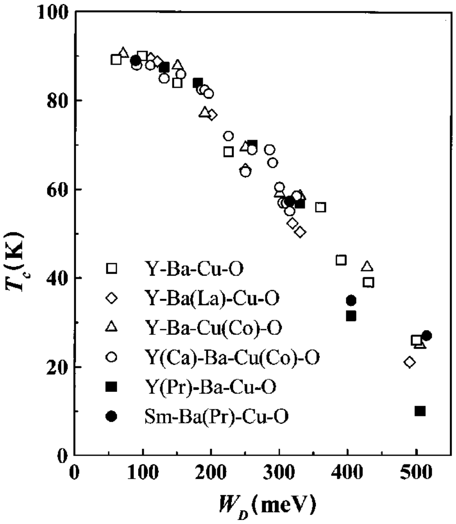

FIG. 7. Correlation between the critical temperature and the effective bandwidth in the $RBa_2Cu_3O_y$ system with different doping. Data for the systems without Pr are taken from Refs. 24, 26 and 68.

V. CONCLUSIONS

In summary, the results obtained and the comparative analysis of the band spectrum transformation in the $SmBa_{2-x}Pr_xCu_3O_y$ and $Y_{1-x}Pr_xBa_2Cu_3O_y$ systems based on the interpretation of the thermopower data in the framework of the narrow-band model allow us to draw the following conclusions.

(i) The substitution by Pr for the Ba site affects the properties of the $RBa_2Cu_3O_y$ system much stronger compared to the Pr→R one resulting in the increasing oxygen content, appearance of an orthorhombic-to-tetragonal transition, a stronger rise of the thermopower, and a faster T_c drop.

(ii) The Pr→Y substitution affects very slightly the total number of electrons in the conduction band due to the fact that the valence of the Pr ion in the $Y_{1-x}Pr_xBa_2Cu_3O_y$ system is close to 3+. To the contrary, in the $SmBa_{2-x}Pr_xCu_3O_y$ system the nonisovalent Pr→Ba substitution results in the hole filling effect, and the Pr ion on the Ba site influences the charge-carrier concentration like other rare-earth impurities placed at the Ba site.

(iii) In both kinds of Pr doping praseodymium has a remarkable effect on the conduction-band transformation inducing the strong band broadening accompanied by the strong states localization. Such an influence can be attributed to the effect of the hybridization between $4f$ states of Pr ion and the conduction-band states. In the case of the Pr→Ba substitution a random ordering of the excess oxygen caused by a higher valence of Pr compared to Ba leads to an additional band broadening and localization of the states.

(iv) Despite a different extent of the Pr influence on the band spectrum and the critical temperature in the

$Y_{1-x}Pr_xBa_2Cu_3O_y$ and $SmBa_{2-x}Pr_xCu_3O_y$ systems, the $T_c(W_D)$ dependence for these systems follows the universal correlation for different substitutions in $YBa_2Cu_3O_y$. The main reason for the superconductivity suppression by praseodymium in both systems is the modification of the band spectrum caused by the Pr introducing into the lattice.

ACKNOWLEDGMENTS

The authors would like to thank Dr. I. Patrina and F. Cairon for the samples preparation and the determination of the oxygen content and the lattice parameters. We are also very grateful to Dr. E. Vladimirskaya for fruitful discussions.

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