Structural, transport, and magnetic properties of $PrBa_{2-x}Sr_xCu_3O_{7-\delta}$

Y. G. Zhao, S. Y. Xiong, Y. P. Li, B. Zhang, and S. S. Fan Department of Physics, Tsinghua University, Beijing 100084, China

B. Yin, J. W. Li, S. Q. Guo, W. H. Tang, and G. H. Rao Institute of Physics, Chinese Academy of Sciences, Beijing 100080, China

D. J. Dong, B. S. Cao, and B. L. Gu Department of Physics, Tsinghua University, Beijing 100084, China (Received 17 March 1997)

Structural, electrical transport, and magnetic properties of polycrystalline samples of $PrBa_{2-x}Sr_xCu_3O_{7-\delta}$ were investigated. The solid solubility limit for Sr in $PrBa_{2-x}Sr_xCu_3O_{7-\delta}$ was found to be about 0.8 and the orthorhombic-to-tetragonal phase transition occurred at x=0.2. With Sr doping, the electrical resistivity reduced abruptly, especially at low temperatures. For the x=0 sample, $\rho(20 \text{ K})/\rho(300 \text{ K}) \sim 10^4$, for the x=0.8 sample, $\rho(20 \text{ K})/\rho(300 \text{ K}) \sim 100$, while for x=1, $\rho(20 \text{ K})/\rho(300 \text{ K}) \sim 3$. In contrast to the aforementioned change, the antiferromagnetic ordering temperature T_N and the effective magnetic moment of Pr ions showed no obvious change indicating their insensitivity to Sr doping. The results are discussed considering the Sr doping induced variation of hybridization between Pr ions and O_{2p} of the CuO₂ planes. [S0163-1829(97)01938-3]

Although great effort has been made towards the understanding of the mechanism of the quenching effect of Pr doping on superconductivity in YBCO and also the anomalously high antiferromagnetic (AF) ordering temperature of Pr ions, it is still an open question.¹ Several models have been proposed, such as hole filling, hybridization, pair breaking, and mixed valence. It seems that hybridization between Pr ions and the O_{2p} state of the CuO₂ plane plays a very important role in the Pr-doping effect. As the hybridization is related to the distance between the Pr ions and oxygen in the CuO_2 plane, a change of this distance will lead to a variation of hybridization and thus a change of the Pr doping effect; therefore, we can study the nature of hybridization. $PrBa_2Cu_3O_7$, as the ending member of $Y_{1-x}Pr_xBa_2Cu_3O_7$, seems to be a good system for this study. The transport property of PrBa₂Cu₃O₇ shows semiconductorlike behavior^{2,3} and the Pr ions order antiferromagnetically at 17 K which is an order higher than that of $T_N(R)$ of other $RBa_2Cu_3O_7$ (R =rare-earth elements).^{4,5} Lai et al. studied the variation of structure and antiferromagnetic Pr ordering in the $Tl(Ba_{1-r}Sr_r)_2PrCu_2O_{7-\delta}$ system (1212 phase) which is an isostructure of PrBa₂Cu₃O₇. Upon Sr doping, the distance between the Pr ions and oxygen in the CuO₂ planes increases although the lattice constants decrease, and both transport properties and $T_N(Pr)$ change a lot.⁶ Considering the similarity between the 1212 and 123 structures, it is reasonable to believe that Sr doping at Ba sites will also lead to the increase of the Pr-O bond length in $PrBa_{2-x}Sr_xCu_3O_7$. In fact, $PrBa_{2-r}Ca_rCu_3O_7$ has been studied for the polycrystalline samples, but the solid solubility limit is too low (~ 0.4). Even so, the transport and magnetic properties show an abrupt change.⁷ Therefore if the solid solubility limit of the dopant is raised, a much greater change in transport and magnetic properties may occur and even the appearance of superconductivity. Pulsed laser ablation (PLA) method is a powerful tool in the fabrication of highvery

 T_c -superconductor thin films, and can greatly increase the dopant solid solubility limit. This has been clearly shown in the preparation of $Y_{1-x}Ce_xBa_2Cu_3O_7$, $Y_{1-x}Tb_xBa_2Cu_3O_7$ thin films which cannot be obtained as single-phased samples in bulk form.⁸ By increasing the dopant amount we can study the transport and magnetic properties of $PrBa_{2-x}Sr_xCu_3O_{7-\delta}$ in a wide range. Tai *et al.* have studied the magnetic properties of $PrBa_{2-x}Sr_xCu_3O_{7-\delta}$ in a wide range. Tai *et al.* have studied the magnetic properties of $PrBa_{2-x}Sr_xCu_3O_y$ single crystals.⁹ Surprisingly, no antiferromagnetic Pr ordering was found, even for the x=0 sample, which is in contradiction with other reports on magnetic properties of $PrBa_2Cu_3O_7$. No other results, to our knowledge, have been found in the literature on the study of $PrBa_{2-x}Sr_xCu_3O_y$. In this paper, we carried out the investigation of the structural, transport, and magnetic properties of $PrBa_{2-x}Sr_xCu_3O_{7-\delta}$.

Polycrystalline samples of $PrBa_{2-x}Sr_xCu_3O_{7-\delta}$ were carefully prepared by the solid state reaction method which is described in detail elsewhere.¹⁰ The sintering temperature was increased with a Sr doping amount increase. Some samples were annealed at 400 °C for 12 h in flowing oxygen in order to compare them with the results of others. For the preparation of thin films on (200) yttrium-stabilized zirconia (YSZ) substrate, the pulsed laser ablation method was used. The structure analysis was performed by powder x-ray diffraction (XRD) using a Rigaku D/max-RB x-ray powder diffractometer with Cu K_{α} radiation. For the x = 0, 0.6 powder samples, the data were collected through step scan with 0.02° /step from 5° -110°. At each point, the data were collected for 10 sec to ensure the intensity. Based on these data, we carried out a Rietveld analysis. The fit is very good as the R factor approaches 3.18 and 3.80, respectively, for the two samples. The electrical resistivity $\rho(T)$ of the samples was measured using the four probe method. Indium was used for the electrical contact. The data was taken within the temperature range of 300-20 K which was achieved by means of a closed He refrigerator (Air Product). Vacuum grease was

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employed to improve the thermal contact between the sample and the cold head of the refrigerator. The measure current was chosen to eliminate the self-heating effect. The dc magnetization for the samples was measured using a superconducting quantum interference device (SQUID) magnetometer (Quantum Design) within the temperature range 4.2–300 K under the magnetic field 1 kOe. The antiferromagnetic ordering temperature T_N was determined from dM/dT curves.

Figure 1 shows the XRD patterns of $PrBa_{2-x}Sr_xCu_3O_{7-\delta}$ samples. It can be seen that the samples are single phased within $x \leq 0.6$, but a minor impurity phase appears in the x = 0.8 sample. So we can deduce that the solid solubility limit is about 0.8 for Sr in $PrBa_{2-x}Sr_xCu_3O_{7-\delta}$, which is a little bit higher than reported by Tai et al. on single crystals of $PrBa_{2-x}Sr_{x}Cu_{3}O_{7}$. Moreover the orthorhombic-totetragonal (O-T) phase transition occurred at about x = 0.2, which can be seen from the splitting of the peak around 46°. This is comparable to that in the $PrBa_{2-r}Ca_rCu_3O_{7-\delta}$ system, where the orthorhombic-to-tetragonal phase transition occurred at x = 0.2.⁷ But considering the oxygen deficiency of our sample prepared in air, the O-T phase transition should occur at a higher doping level for the fully oxygenated sample (for example, prepared in oxygen) because oxygen deficiency also reduces the orthorhombicity. This has been demonstrated by the increase of peak splitting at 46° after oxygen annealing of the samples. As the ion radius of Sr^{2+} is smaller than that of Ba^{2+} , Sr doping will lead to the contraction of unit cell and locally the increase of the distance between Pr ions and CuO₂ planes. This has been demonstrated in the $Tl(Ba_{1-x}Sr_x)_2PrCu_2O_{7-\delta}$ system.⁶ Our Rietveld analysis for the x=0, 0.6 samples shows that upon doping, lattice constants a, c decrease from 0.39038, 1.16835 nm to 0.38827, 1.16269 nm, while the Pr-O distance increases from 0.23650 to 0.23768 nm. Both the x=0, 0.6samples are in the tetragonal phase as they have been treated at 400° in the air. It has been shown that the orthorhombicity of PrBa₂Cu₃O₇ is very small compared with that of YBa₂Cu₃O₇. So it is easy to become tetragonal when treated in the air. It has been shown that oxygen content has little influence on the bond length of the rare-earth element and oxygen in the CuO_2 plane.¹¹ The increase of the Pr-O distance upon Sr doping comes from the decrease of the chemical pressure on CuO₂ planes of Sr compared with Ba. With Sr doping, the nearest neighbor (NN) of Sr will come closer to Sr, while the next-nearest neighbor (NNN) will come less close to Sr, i.e., the atoms in the unit cell do not move uniformly. This results in the increase of the bond length of Pr-O (the CuO₂ plane is the NN of Sr and Pr is the NNN of Sr). Our result shows that the Pr-O bond length indeed increases with Sr doping. In order to raise the doping amount, we prepared the PrBaSrCu₃O₇ thin films. Figure 2 shows the XRD patterns of the target and thin film. It can be seen that there are some impurity phases in the target, while the XRD pattern of the thin film shows the *c*-axis aligned 123 phase. For further doping, more work is needed to optimize the fabrication.

The variation of electrical resistivity ρ with temperature T for PrBa_{2-x}Sr_xCu₃O_{7- δ} is shown in Fig. 3. An abrupt change occurred upon Sr doping. For the x=0.8 sample, $\rho(20 \text{ K})/\rho(300 \text{ K}) \sim 100$, while for the x=0 sample,



FIG. 1. X-ray-diffraction patterns for x = 0, 0.1, 0.2, 0.6, and 0.8 samples of PrBa_{2-x}Sr_xCu₃O_{7- δ}. The dots in the XRD pattern of the x=0.8 sample shows the impurity phase.

 $\rho(20 \text{ K})/\rho(300 \text{ K}) \sim 10^4$. For the x=1 thin film, $\rho(20 \text{ K})/\rho(300 \text{ K}) \sim 3$ was reached. Metallic conductivity or even superconductivity can be expected for further doping. Upon doping the low-temperature resistivity changes more abruptly than that of the room-temperature resistivity. This can be understood considering the transport mechanism at low temperatures,¹² i.e., variable range hopping (VRH) ρ $\sim \rho_0 \exp(T_0/T)^{1/4}$, where ρ_0 , T_0 are sample related param-



FIG. 2. XRD patterns of $PrBaSrCu_3O_7$ for target (a) and thin film (b). An asterisk indicates the impurity phases.

eters. Thus at low temperatures, $exp(T_0/T)^{1/4}$ will show a remarkable change as a result of the doping induced variation of T_0 . The sensitivity of the low-temperature resistivity is also reflected in the scatter of the low-temperature resis-tivity data published in literature.^{4,12–15} This may be related to the different oxygen content and interconnection between grains. Thus we may expect a lower low-temperature resistivity for a high-quality sample (high oxygen content and good connection between grains). Lopez-Morales et al. studied the effect of oxygen content on the electrical transport properties of PrBa₂Cu₃O_{7- δ} and found that the $\rho \sim T$ curve shifts upward with decreasing oxygen content,¹⁵ so oxygen content variation has the same influence on both lowtemperature resistivity and room-temperature resistivity. In the literature, the resistivity at room temperature are consistent while the resistivity at low-temperature scatters. The scatter of low-temperature resistivity is most likely a result



FIG. 3. Temperature dependence of electrical resistivity ρ for $\Pr Ba_{2-x}Sr_xCu_3O_{7-\delta}$ with x=0 (\blacksquare), 0.1 (\bigcirc), 0.6 (\blacktriangle), 0.8 (\diamond), and 1.0 (\bigtriangledown) (thin film).



FIG. 4. Temperature dependence of dc magnetization M(T) for $PrBa_{2-x}Sr_xCu_3O_{7-\delta}$ with x=0 (\blacksquare), 0.2 (\bigcirc), and 0.6 (\bullet).

of the connection between grains and also the presence of possible impurity phases. Unlike the variation of resistivity with doping in $PrBa_{2-x}Sr_xCu_3O_{7-\delta}$, the resistivity does not show monotonic variation with doping in $PrBa_{2-x}Ca_xCu_3O_{7-\delta}$, in which the resistivity begins to increase for the x=0.4 sample.⁷ This has been explained as being due to the atomic disorder effect and structural change,⁷ and may also be related to impurity phases and grain connections.

Figure 4 shows the result of dc magnetization for the oxygen annealed samples. The antiferromagnetic ordering temperature T_N of Pr ions was determined by the midpoint of the upturn in dM/dT curves (Fig. 5). For the undoped sample, the T_N value is consistent with the published results obtained from the samples prepared in oxygen.^{7,15–18} Surprisingly, T_N does not show an obvious change with Sr doping, in contrast to the variation of structure and transport properties. At present, the detailed mechanism of the antiferromagnetic ordering of Pr ions is not very clear. It is commonly believed that the superexchange interaction between Pr ions via oxygen atoms in the CuO₂ planes is responsible for the anoma-



FIG. 5. Variation of dM/dT with temperature for $PrBa_{2-x}Sr_xCu_3O_{7-\delta}$.

lously high T_N of the Pr ions. The hybridization between the Pr 4f and O 2p states is also crucial to the quenching effect of Pr doping on the superconductivity of YBCO. The present results indicated that the T_N of the Pr ions is not as sensitive as transport properties to the hybridization. Yang et al. have shown that the T_N of the Pr ions does not show apparent variation upon Ca doping in $PrBa_{2-x}Ca_xCu_3O_7$ within $0 \le$ $x \leq 0.2$. Further doping leads to a reduction of T_N .⁷ For the 1212 phase materials such as $Tl(Ba_{1-x}Sr_x)_2PrCu_2O_{7-\delta}$ and $Pr(Ba_{1-x}Sr_x)_2Cu_2NbO_{8-y}$ [the one-dimensional (1D) CuO chain in $PrBa_{2-x}Sr_xCu_3O_{7-\delta}$ has been replaced by a TIO chain and a NbO plane, respectively, in these two samples],^{6,16} the $T_N(Pr)$ is very sensitive to Sr doping. This is in constrast to the $PrBa_{2-x}Sr_xCu_3O_{7-\delta}$ system studied here. This shows the role of the 1D CuO chain in determining the anomalous AF ordering of Pr ions. It has been shown that doping in the 1D CuO chain strongly affects the $T_N(Pr)$,¹⁷ while doping at the CuO₂ plane site shows no effect on $T_N(Pr)$.^{17,18} So the $T_N(Pr)$ is determined by the unit cell as a whole. Our result does not support the result of Tai et al. on the susceptibility measurement of $PrBa_{2-x}Sr_{x}Cu_{3}O_{7}$ single crystal,⁹ in that they did not find the slope change of χ related to Pr ions AF ordering even in the PrBa₂Cu₃O₇ sample which is in contradiction with other reports which have been well established.^{4,19} Using the Curie-Weiss law $\chi = \chi_0 + C/(T - \theta)$ to fit the experimental data, where θ is the paramagnetic Curie-Weiss temperature, χ_0 is a sum of temperature-independent terms, and $C = N \mu_{eff}^2 / 3k_B$ $(\mu_{\rm eff}$ is the effective magnetic moment of paramagnetic ions, k_{R} is the Boltzmann constant, and N is the concentration of paramagnetic ions), we can deduce the effective magnetic moment μ_{eff} for x = 0, 0.2, 0.6 samples to be $2.64 \mu_B$, $2.58\mu_B$, $2.59\mu_B$, respectively. No obvious change of $\mu_{\rm eff}$ occurred. It has also been shown that the effective magnetic moment of the Pr ions is independent of x and has an average value of $2.6\mu_B$ in the $Y_{1-x}Pr_xBa_2Cu_3O_6$ system.¹⁸ The magnetic moment of Pr ions lies between that of the free Pr^{3+} (3.58 μ_B) and Pr^{4+} (2.54 μ_B) ions. This has been explained considering the crystal field effect (CFE) on the Pr³⁺ ions.^{20,21} Notice that the starting point of the upturn in Fig. 5 increases with Sr doping and also the amplitude of the upturn decreases with Sr doping. This needs further study.

The variation of electrical transport and magnetic properties of $PrBa_{2-x}Sr_xCu_3O_{7-\delta}$ with Sr doping can be explained considering the Sr doping induced variation of hybridization between the Pr ions and O_{2p} of the CuO₂ planes. As the distance between the Pr ions and CuO₂ planes increases, the hybridization between them decreases. Thus the localization length of the carriers (holes), which have been localized due to hybridization, increases with Sr doping, so an abrupt change occurs in the electrical transport property. At low temperatures, the transport behavior is dominated by the VRH mechanism,²² $\rho(T) = \rho_0 \exp(T_0/T)^{1/4}$, where T_0 $=\beta/[k_B N(0)d^3]$, N(0) is the density of states at the Fermi level, d is the localization radius of states near the Fermi level, k_B is Boltzmann's constant, and β is a numerical coefficient. Sr doping leads to the decrease of T_0 and thus the abrupt change of resistivity at low temperature. At higher temperatures, the electrical transport behavior is dominated by another mechanism which is less dependent on doping.¹⁴



FIG. 6. Electrical resistivity ρ versus $T^{-1/4}$ for $PrBa_{2-x}Sr_xCu_3O_{7-\delta}$ samples.

So the electrical resistivity at room temperature changes with Sr doping much more slowly than that at low temperatures. In Fig. 6, we show the electrical resistivity $\ln \rho$ versus $T^{-1/4}$ for the $PrBa_{2-x}Sr_xCu_3O_{7-\delta}$ samples. We also tried the electrical resistivity $\ln \rho$ versus $T^{-1/3}$ (i.e., 2D variable range hopping conductivity) and it gives similar curves. This means that we can not distinguish between 2D and 3D VRH. It has already been pointed out that it is hard to distinguish between a $T^{-1/4}$ and a $T^{-1/3}$ dependence of ln ρ (VRH in 3D or in 2D) for PrBa₂Cu₃O₇, unless the temperature range extends over at least one order of magnitude which is not satisfied in this compound.²³ For the critical temperature below which the VRH law is satisfied, values of 150 and 100 K have been reported, respectively.^{12,23} This discrepancy may be related to the sample difference. Our result shows that this temperature increases with Sr doping and almost reaches room temperature for the x = 1 sample. In the experiment we noticed that a small temperature difference between the sample and the temperature sensor is present at low temperature. Currently most people use the 3D VRH model to explain the transport properties of PrBa₂Cu₃O₇ and related materials. Here we also use the 3D VRH model to analyze our result, and the 2D VRH model will not change the result qualitatively. By fitting the curves in Fig. 6, we obtained T_0 and then taking¹² $N(0) = 10^{21}$ /cm³ eV, $\beta = 20$ and assuming that N(0) does not change with doping, we obtained the localized radius d and its reciprocal. The T_0 value for the x=0 sample is about 4×10^5 K, which is very close to the 1.8×10^5 K result reported by Fisher *et al.*²³ Figure 7 shows



FIG. 7. Variation of the localization radius *d* and its reciprocal 1/d with Sr doping for the PrBa_{2-x}Sr_xCu₃O_{7- δ} samples.

the doping dependence for of d and 1/d $PrBa_{2-x}Sr_xCu_3O_{7-\delta}$. By extrapolating, it can be seen that 1/d will go to zero around x=1.1, which means that d diverges. This implies that $PrBa_{2-x}Sr_xCu_3O_{7-\delta}$ will become a metal or even a superconductor owing to the delocalization the carriers. For the magnetic property of of $PrBa_{2-x}Sr_{x}Cu_{3}O_{7-\delta}$, the situation may be a little bit complicated. The AF ordering of Pr ions in PrBa₂Cu₃O₇ shows a series of anomalies. For example, its 17 K T_N is about two orders of magnitude higher than expected if one scales the T_N of GdBa₂Cu₃O₇ (T_N =2.2 K) assuming either dipolar interaction or Ruderman-Kittel-Kasuya-Yosida (RKKY) exchange. For conventional AF, a few T of external magnetic field is expected to suppress its T_N by a few degrees K, while T_N of PrBa₂Cu₃O₇ remains unchanged under the magnetic field up to 9 T.⁴ The dc susceptibility increases monotonically with decreasing temperature below T_N in PrBa₂Cu₃O₇ instead of showing a peak at T_N in conventional AF. It is commonly believed that superexchange interaction between Pr ions via oxygens in the CuO₂ planes is responsible for the anomalous high T_N and related phenomena. The superexchange interaction is a short-range interaction. This has been shown in T_N suppression due to dilution of Pr ions by doping at Pr sites. For $PrBa_{2-r}Sr_rCu_3O_{7-\delta}$, Sr doping lead to an increase of the Pr-O bond length (the oxygen sits in the CuO₂ planes) and also a decrease of the Pr-Pr distance. The former factor decrease T_N , while the latter may increase T_N . So the balance of the two factors may lead to the insensitivity of T_N to doping. The bond angle of Pr-O-Pr, which decreases with Sr doping, should also be considered. The insensitivity of T_N to doping was also shown in $PrBa_{2-x}Ca_xCu_3O_{7-\delta}$ with x <0.2, while further doping leads to an abrupt decrease of T_N . Generally speaking, $T_N(Pr)$ is very sensitive to structural variation, especially in the *c* axis. For example, T_N changes very slowly with doping for $Pr_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$, consistent with the minor structural variation, and doping is just a dilution effect. For $PrBa_{2-x}Ca_xCu_3O_{7-\delta}$, T_N decreases much more quickly with doping than that for $Pr_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$, together with remarkable structural variation. The role of structural variation in suppressing T_N can also be illustrated in $PrBa_2Cu_{3-x}M_xO_{7-\delta}$ (M = Zn,Co,Ni,Fe) systems, in which T_N remains unchanged for Zn doped $PrBa_2Cu_3O_7$ and shows an abrupt change for Co, Ni, and Fe doped samples. Very recently, Boothroyd *et al.* found that the AF ordering of Pr ions interacts with Cu sublattices indicating the complicated mechanism of AF ordering of the Pr ions.²⁴

In summary, we have studied the effect of Sr doping at Ba sites on structural, electrical transport, and magnetic properties of $PrBa_2Cu_3O_{7-\delta}$. An orthorhombic-to-tetragonal phase transition occurs at x = 0.2 and the solid solubility limit of Sr was found to be 0.8. Electrical resistivity abruptly decreases upon Sr doping. In contrast, the magnetic property show no obvious change. The results were explained considering the Sr doping induced variation of hybridization between Pr ions and O_{2p} of the CuO₂ planes. Further doping may lead to much more change and even the possible appearance of superconductivity.

This work was supported by the China R&D Center for Superconductivity. One of us (Y.G.Z.) is thankful for the support of the Foundation for Young Scientists of Tsinghua University.

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