LETTER TO THE EDITOR

Evidence for Retarded Pr f Hybridization and T_c Suppression in $Y_{1-x}Pr_xSr_2Cu_{2.85}Re_{0.15}O_7$

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We report on the preparation, X-ray diffraction, ac susceptibility, resistivity, and thermopower of $Y_{1-x}Pr_xSr_2Cu_{2.85}Re_{0.15}O_7$. We find that superconductivity is sustained up to a Pr concentration of 70%, which is greater than the 55% normally found in the $Y_{1-x}Pr_xBa_2Cu_3O_7$ system. It is proposed that the presence of Sr retards the Pr f hybridization and the T_c suppression. It is pointed out that a better knowledge of structural and defect chemistry of Pr-containing cuprates is essential before applying any definite model to account for the data, as was also proposed earlier by R. Fehrenbacher and T. M. Rice (*Phys. Rev. Lett.* **70**, 3471, 1993). © 1995 Academic Press, Inc.

Among the various rare-earth-substituted $YBa_2Cu_3O_{6+z}$ (YBC), the properties of $Y_{1-x}Pr_xBa_2Cu_3O_{6+z}$ (YPB) have been extensively studied but are the least understood (1). In contrast to other trivalent rare earths, Pr destroys superconductivity in this compound for $x >$ 0.55, and for $x = 1$, an antiferromagnetic transition is observed at 17 K. The value of x_{cr} for which T_c goes to zero depends on the specific rare earth (2). To interpret some of these results, mechanisms involving hole filling and/or pair breaking have been proposed. In the hole-filling model (3, 4), Pr adopts a valence of 4+ and the extra electron missing from the Y site may transfer to the Cu–O planes to decrease the hole density and hence the T_c. However, the valence of Pr was found to be close to 3+ (for all $x > 0$) from $M_{4,5}$ X-ray absorption edge spectra (5), valence-band resonant photoemission (6), and coulometric (7) experiments. According to the pair-breaking model (8), the decrease in T_c results from the interaction

of extended Pr^{3+} orbitals with the charge carriers in the Cu–O planes.

In order to gain further insight into this problem, we felt it would be interesting to look for other substitutions, such as the Sr analog of the $Y(Pr)Ba_2Cu_3O_{6+z}$ system, hoping that the smaller size of Sr^{2+} might modify the hold-filling/pair-breaking mechanism and thereby change the superconducting properties of the system. But, it is well known (9) that Sr substitution for Ba does not lead to single-phase materials. It was shown (11, 12), however, that $YSr_2Cu_{3-y}M_yO_{6+z}$ has a stable perovskite structure for a wide variety of M dopants (3d, 4d, and 5d). Of these, we were interested in M = Re and report on the behavior of Pr in $Y_{1-x}Pr_xSr_2Cu_{2.85}Re_{0.15}O_{6+z}$.

The polycrystalline samples have been prepared by solid state sintering of the respective oxides or carbonates. Y_2O_3, Pr_2O_3, $SrCO_3$, ReO_2, and CuO were thoroughly mixed in required proportions and calcined at 950°C in air for a period of 12–18 hr. The resulting product was ground, mixed, pelletized, and heated in air at 980°C for a period of 16–24 hr. This was repeated twice. The pellets were annealed under oxygen at 1000°C for a period of 24 hr and furnace cooled.

X-ray diffraction of the samples revealed a tetragonal symmetry. One impurity peak pertaining to $SrCuO_2$ was identified. The a parameter increased gradually as a function of Pr concentration (Fig. 1). In contrast, the c/a parameter decreased gradually. In YPB, both an increase and a decrease in c have been reported (1). However, in the present case, the volume was found to increase as a function of $x(Pr)$, as reported in the case of YPB. Energy dispersive X-ray analyses revealed a fairly uniform distribution of Pr and the measured composition was close to that of the nominal composition. The oxygen content was found to decrease from about 6.95 for $x = 0$ to about 6.80 for $x = 0.6$. The real (χ') and imaginary (χ'') parts of the ac susceptibility of the samples with $x(Pr) = 0$, 0.2, 0.4,

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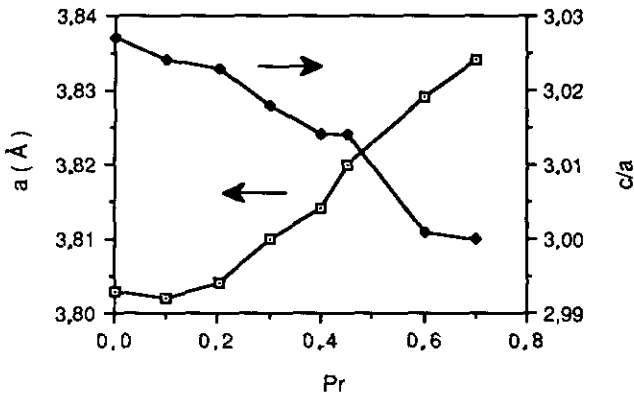
FIG. 1. Lattice parameters a and c/a of $Y_{1-x}Pr_xSr_2Cu_{2.85}Re_{0.15}O_{6+z}$. Lines are drawn as visual guides.

0.63, and 0.7 are shown in Fig. 2 as a function of temperature. An ac field of 0.11 Oe at a frequency of 1500 Hz was used. The data clearly indicate that the superconductivity is not destroyed for $x(Pr) > 0.55$, the critical value at
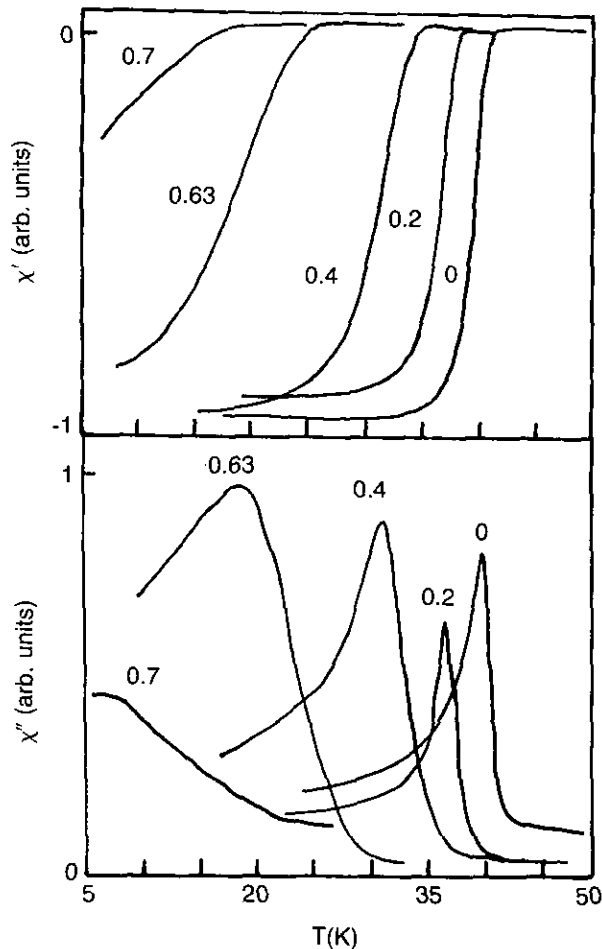

FIG. 2. Real (top) and imaginary (bottom) parts of ac susceptibility of $Y_{1-x}Pr_xSr_2Cu_{2.85}Re_{0.15}O_{6+z}$ as a function of temperature.
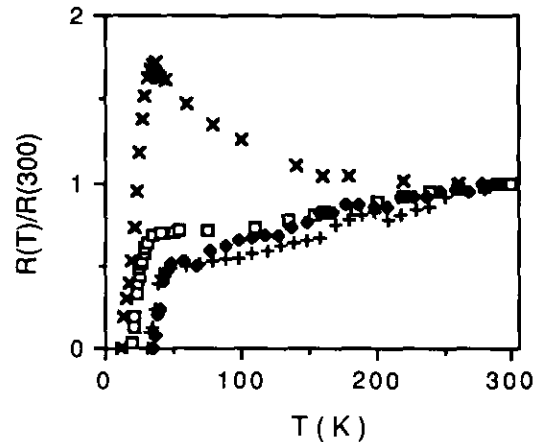

FIG. 3. Normalized resistivity of $Y_{1-x}Pr_xSr_2Cu_{2.85}Re_{0.15}O_{6+z}$ as a function of temperature: ($\blacklozenge$) $x = 0$; ($+$) $x = 0.2$; ($\square$) $x = 0.4$; and ($\times$) $x = 0.7$.

which T_c goes to zero in the YPB system. In Fig. 2, $\chi' = -1$ represents the signal of a fully oxidized $YBa_2Cu_3O_7$ superconductor prepared in our laboratory. Our samples and the $YBa_2Cu_3O_7$ sample are of similar size and shape. Thus, we estimate about 20 to 25% shielding effect for the $x = 0.7$ sample compared to $YBa_2Cu_3O_7$. The intergranular coupling gets weaker as x increases, especially for $x > 0.6$, as reflected by an increase in the width of the χ'' peaks. We note here that quenching of the samples from 1000°C followed by oxygen annealing at 600°C resulted in an increase in the χ' signal and a decrease in the width of χ'', especially for $x > 0.6$. For $x \geq 0.75$ no superconductivity was observed at temperatures down to 5 K.

The superconducting transitions were also confirmed by resistivity (ρ) data (Fig. 3). For all the samples with $x < 0.63$, the normal state resistivity decreased with T whereas for $x = 0.7$, ρ increased, starting from about 120 K, reaching a maximum at around 25 K before dropping to zero. The T_c ($\rho = 0$) obtained from these data coincided fairly well with those obtained from ac susceptibility measurements. The resistivity at 300 K increased gradually from around 1.2 m ohm cm for $x = 0$ to about 8 m ohm cm for $x = 0.7$.

The thermopower (S) of the samples increased as T increased, showing a broad maximum before reaching zero at $T = Tc$, as is commonly observed in most of the other cuprate superconductors. All the samples showed a positive value, indicating that holes are majority carriers. Further, S (at 300 K) increased with x (Fig. 4a). Following Obertelli et al. (13) our samples can be considered underdoped compared to $YBa_2Cu_3O_7$ and further, the hole density decreased as a function of x. The temperature behavior of S will be discussed elsewhere.

The above data clearly indicate that Pr does not suppress superconductivity in the present system for con-
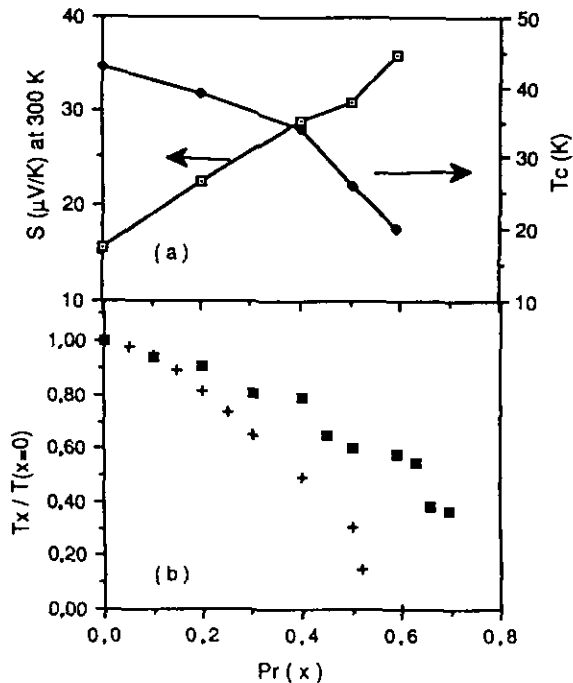
indication of localization of holes, leading to the absence of superconductivity. Further, polarized optical spectra on detwinned $PrBa_2Cu_3O_7$ single crystals showed that it was difficult to dope mobile holes into the $Cu-O_2$ plane, making it an insulator [18]. Finally, Mössbauer data obtained on [170]Yb^{3+}-substituted YPB suggested that though the superconductivity was suppressed at x_{cr} when the Pr^{3+} became magnetically ordered, the suppression was not directly due to this ordering but rather due to changes produced by the Pr^{3+} on the $Cu-O_2$ planes [19].

Several theoretical models were proposed to account for a part of the data discussed above on the YPB system [20–22]. Though these models would account for some of the data discussed above, they cannot quantitatively explain our data. However, it was pointed out that the extreme sensitivity of the 1D chains and the $Pr^{III}-Pr^{IV}$ mixed valent state to O vacancies and other defects may play a role [22]. Three results seem to support this viewpoint. We did observe that superconductivity can be induced or the strength of the signal can be increased in our samples for $x(Pr) > 0.6$ by quenching the samples from 1000°C and then annealing under oxygen, as mentioned earlier. This might be due to a proper organization of O vacancies in the basal plane. Second, thin films but not bulk samples of $Pr_{0.5}Ca_{0.5}Ba_2Cu_3O_{6+z}$ show superconductivity [23]. Third, it was shown [24] recently by optimizing the growth conditions of single crystals of YPB that T_c could be increased by about 20 K, compared to polycrystalline samples for $x = 0.5$. Finally, to understand the role played by Sr, we examine the data on the nonsuperconducting samples of the $TiBa_{2-y}Sr_yPrCu_2O_{6+z}$ system [25]. It was found that T_N decreased from 8 K for $y = 0$ to around 3.6 K for $y = 1$, due to the modification of Pr f hybridization resulting from the presence of the smaller Sr. In our case it is quite possible that the AF interaction of Pr was much decreased due to a weakening of Pr f Cu–O_2 hybridization even up to a concentration of 70% of Pr, preserving superconductivity. Another possibility of weakening this AF interaction might arise from the Cu chain being substituted by Re, as was observed [26] in the case of other chain substitutions, such as Ga, Co, and Fe, in $PrBa_2Cu_3O_7$. Specific heat and magnetic measurements are being planned to examine this interesting aspect. It is interesting to note that recently granular superconductivity was reported [27] in $PrBa_2Cu_3O_7$ ($T_c = 90$ K) films. It was proposed that in such films the migration of Pr to the Ba site is reduced to a great extent [28]. Such an argument may also be considered to explain our data. As pointed out [28], there is some evidence for as much as 10% of Pr substituting at the Ba site.

In conclusion, we have shown that, by a suitable selection of the parent compound $YSr_2Cu_{2.85}Re_{0.15}O_{6+z}$ and the proper heat treatment, the T_c depression by Pr was retarded and superconductivity could be sustained for up to

FIG. 4. (a) Thermoelectric power (S) at 300 K and T_c of $Y_{1-x}Pr_x$ $Sr_2Cu_{2.85}Re_{0.15}O_{6+z}$. (b) Normalized T_c as a function of Pr. (■) $Y_{1-x}Pr_x$ $Sr_2Cu_{2.85}Re_{0.15}O_{6+z}$; (+) $Y_{1-x}Pr_xBa_2Cu_3O_{6+z}$.

centrations reaching 70%, which is much larger than the x_{cr} (0.55) observed in the YPB system. In fact, $T_c(x)/T_c(x = 0)$ decreases more rapidly starting from x as low as 0.2 in the case of the YPB system (Fig. 4b). We now present a short discussion of our results in the light of certain models.

In the case of YPB, the decrease in T_c as x increased was accompanied [4] by a rapid increase in S. This was attributed to a progressive band filling and to a rapid decrease in the number of holes per Cu atom. In our system, our data show (Fig. 4a) that S increased almost linearly with x (Pr) up to $x = 0.6$. On the other hand, the decrease in T_c was nonlinear for $x > 0.4$. Hence, the decrease in T_c for $x > 0.4$ cannot be due only to a regular decrease in the number of holes. This might indicate (for $x > 0.4$) a strong scattering of carriers and/or localization of holes. Since Pr is known [14] to occupy only Y sites, the decrease in T_c should be strongly related to an increase in hybridization of Pr f orbitals with those of $Cu-O_2$ orbitals.

It has been argued that T_c depression as a function of z in YPB is similar to that observed in $YBa_2Cu_3O_{6+z}$ [15]. However, it was pointed out recently that the NQR spectral features of YPB are quite different from those of the oxygen-depleted $YBa_2Cu_3O_{6+z}$ [16]. The contribution of the Cu wavefunction to the quadrupole interaction is largely changed in the $Cu(2)$ site in the Pr system compared to other cuprates [17]. This was interpreted as an

70% of Pr in this cuprate. This concentration is much higher than that (55%) normally reported by several others for the YBaCuO matrix. It is suggested that Pr f hybridization is weakened by Sr substitution. We believe that before identifying the behavior of Pr with any specific model (pair breaking, hole filling), better knowledge of structural and defect chemistry of Pr-containing cuprates is essential because of the extreme sensitivity of Pr f hybridization to structural parameter defects and vacancies, as was also suggested earlier (22).

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