# Transport properties of the oxides $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ ($0 \le x \le 1$): Effects of band filling and lattice distortion on superconductivity

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The oxides with composition $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ ($0 \le x \le 1$) are characterized by x-ray diffraction, resistivity ($\rho$), and thermoelectric power ($S$) measurements. X-ray diffraction shows an orthorhombically distorted perovskite structure for all compositions, the pseudotetragonality increasing with $x$. The substitution of the tetravalent Pr for the trivalent Y atom increases the band filling in these materials. As a consequence, the superconducting transition temperature is progressively decreased with increasing $x$, and $S$ significantly increases. Thermopower and resistivity measurements indicate that these oxides have relatively narrow bands and that the electronic correlations dominate their properties.

The recent discovery of superconductivity above 30 K by Bednorz and Müller[1] in a layered perovskite oxide of La, Ba, and Cu, followed by the discovery of superconductivity above 90 K by Wu, Chu, and co-workers[2] in a Y-Ba-Cu oxide, later identified[3,4] as an oxygen-deficient orthorhombically distorted perovskite $Y_1Ba_2Cu_3O_{7-\delta}$, has spurred large activity in the field of high-temperature superconductors. Subsequent work showed that in $YBa_2Cu_3O_{7-\delta}$, the substitution of trivalent rare earths such as La, Nd, Sm, Eu, Gd, Dy, Ho, Er, Tm, Yb, and Lu for Y,[5,6] even if they are magnetic, do not affect the superconductivity in this type of compound, while tetravalent rare earths such as Ce or Pr destroy superconductivity and give compounds with conductivity showing an activated behavior in polycrystalline samples.

Chemical substitution of different atoms[5-9] as well as band-structure calculations on these oxides[10,11] provide evidence that the segregated Cu−O layers and chains are key features of the high-temperature superconductivity in these compounds.

In order to achieve a better understanding of the role of the rare-earth atom in high-temperature superconductivity, and to enlighten their mechanisms, we have prepared the oxides with compositions $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ ($0 \le x \le 1$) and performed a detailed characterization of their physical properties as a function of $x$. In this paper, special attention is paid to thermoelectric power in addition to electrical resistivity and x-ray diffraction. Thermopower measurements provide not only information complementary to resistivity, but they are also a more direct probe to the intrinsic properties of a polycrystalline material like these ceramics. In fact, as a zero-current measurement, thermopower is less sensitive than the electrical resistivity to the grain boundary effects always present in granular materials.

All samples with compositions $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ ($0 \le x \le 1$) were synthesized by the solid-state reaction of the appropriate amounts of $Y_2O_3$ (99.99%, Ventron), $Pr_2O_3$ (99.9%, Pechiney-St. Gobain), $BaCO_3$ (99.5%, Carlo Erba RPE-ACS), and CuO (99.999%, Ventron). A mixture of fine powders of the starting materials was first fired as a pellet in air of 850 °C for 12 h, followed by slow cooling in the furnace. Then this pellet was again milled in an agate vial and repressed as a pellet with 12 mm diameter and ~1 mm thickness at 8 kbar and reheated at 850 °C during 12 h in air. Finally, the samples were submitted to a heat treatment under pure oxygen atmosphere, 16 h at 600 °C, and then cooled at a rate of 30 °C/h.

The observed x-ray diffraction powder patterns for all of the compositions can be indexed to the orthorhombic structure similar to the previously described $YBa_2Cu_3O_{7-\delta}$ (Refs. 3 and 4) with just a slight expansion of the cell dimensions, particularly the $a$ parameter that approaches $b$ and $c/3$ with increasing Pr content. There is no evidence of any other phrases which, if present, are below 5%.

Resistivity measurements were performed in bar-shaped samples approximately $5 \times 1.5 \times 1.5$ mm$^3$ cut from the pellets, by a standard four-probe technique, using a lock-in amplifier (EG&G/PAR 5301) at a low frequency (27 Hz). Four in-line silver electrodes were evaporated onto the sample, and silver wires were glued to them with platinum paint (Demetron 308A). The current density was approximately $10^2$ mA/cm$^2$ and the resolution of the voltage measurements was $10^{-8}$ V.

Thermoelectric power was measured by a slow ac (~0.01 Hz) technique[12] using a previously described apparatus[13] presently operated automatically under computer control.[14] The small elongated samples approximately $4 \times 1 \times 0.5$ mm$^3$, with evaporated silver contacts at the ends, were mounted with platinum paint between two 25 $\mu$m, high-purity gold foils (99.99% Goodfellow Metals) connected to two thermal reservoirs of quartz inside a vacuum chamber. The temperature gradients used were always smaller than 2 K and were measured using either gold-0.7 at.% Fe versus Chromel or copper versus Constantan thermocouples, depending on the temperature range. The experimental conditions used enabled us to

have measurements with a resolution better than 0.1% or 0.1 $\mu V/K^{-1}$, whichever is the greater. Absolute thermoelectric power was calculated after correction for the absolute thermoelectric power of the gold leads, using the data of Huebner.[15]

In Fig. 1, the resistivity measurements are plotted as a function of temperature for different degrees of substitution of Pr in $YBa_2Cu_3O_{7-\delta}$. Their main parameters are summarized in Table I. The samples with $x$ up to 0.5 all display metallic behavior in electrical resistivity, down to

a critical temperature, which decreases with $x$, where a sudden drop to zero resistance ($\rho < 10^{-6}$ $\Omega$ cm) is observed. The compositions up to $x = 0.4$ have a temperature dependence of resistivity similar to pure $YBa_2$-$Cu_3O_{7-\delta}$, decreasing in all of them approximately linearly with decreasing temperature. For $x = 0.5$, a sudden drop to zero resistance is observed at $\sim 30$ K, preceded by a temperature region (40–80 K) with negative $d\rho/dT$. The effect of substitution of Pr by Y for $x$ up to 0.5 gives a minor increase in room-temperature resistivity, followed
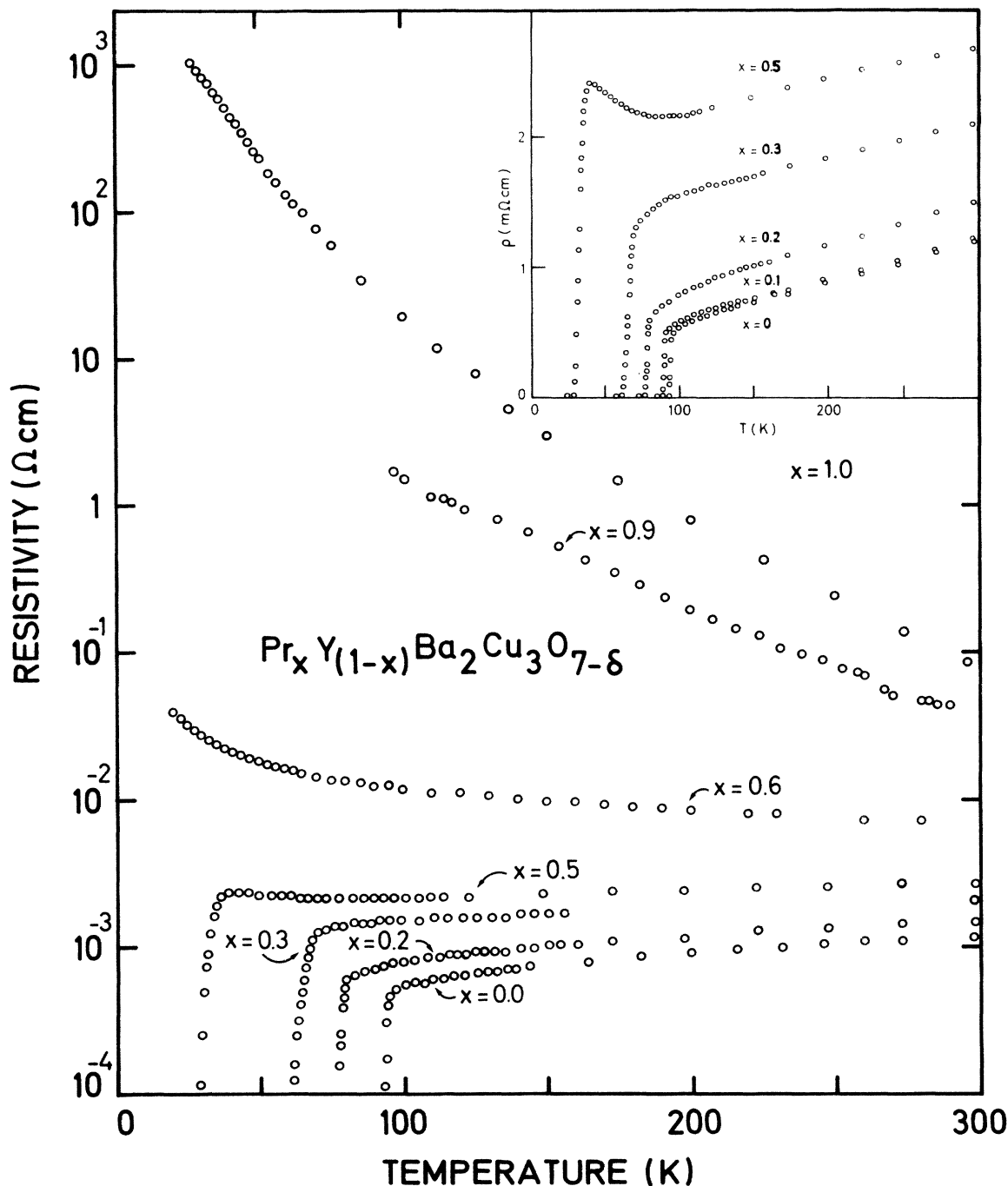


FIG. 1. Electrical resistivity as a function of temperature for $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ ($0 \le x \le 1$). The inset shows the detail for $x \le 0.5$ in a linear scale.

TABLE I. Transport parameters for $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$. $T(10\%)$ and $T(90\%)$ represent temperatures for 10% and 90% resistance drop, respectively.

| $x$ | $\rho(300\ K)$ (m$\Omega$ cm) | $T(10\%)$ (K) | $T(90\%)$ (K) | $T_{\rho=0}$ (K) | $T_{S=0}$ (K) |
|---|---|---|---|---|---|
| 0.0 | 1.18 | 92.9 | 94.4 | 92.6 | 91.2 |
| 0.05 | 1.20 | $\cdots$ | $\cdots$ | $\cdots$ | 91.0 |
| 0.1 | 1.23 | 89.0 | 90.8 | 88.6 | 86.2 |
| 0.2 | 1.52 | 77.2 | 79.6 | 76.4 | $\cdots$ |
| 0.3 | 2.10 | 61.9 | 68.0 | 60.5 | $\cdots$ |
| 0.4 | 2.50 | 46.0 | 57.2 | 44.0 | 42.5 |
| 0.5 | 2.7 | 29.2 | 38.0 | 28.7 | 30.0 |
| 0.6 | 5.5 | $\cdots$ | $\cdots$ | $\cdots$ | $\cdots$ |
| 0.7 | 15.0 | $\cdots$ | $\cdots$ | $\cdots$ | $\cdots$ |
| 0.8 | 27.0 | $\cdots$ | $\cdots$ | $\cdots$ | $\cdots$ |
| 0.9 | 61.0 | $\cdots$ | $\cdots$ | $\cdots$ | $\cdots$ |
| 1.0 | 85.4 | $\cdots$ | $\cdots$ | $\cdots$ | $\cdots$ |

by a more significant increase, of approximately one order of magnitude from $x = 0.6$ to $x = 1.0$. This relatively smooth variation of the electronic properties with the degree of substitution of Praseodymium contrasts with the drastic effect of substitution of other transition-metal atoms like Ni or Fe for Cu, that in much smaller amounts ($\sim 3\%$) destroy superconductivity.[9] For $x \geq 0.6$, the resistivity shows an activated behavior from room temperature down to 2 K (and no signs of superconductivity are seen in the magnetic susceptibility measurement down to this temperature). However, as it will be shown by the thermopower results, the activated regime of resistivity is not intrinsic from these compositions. It most probably reflects the resistance of the interparticle contacts or a hopping mechanism of transport, and it cannot be concluded that the oxides with $x \geq 0.6$ are semiconductors with a gap in the density of states at the Fermi level.

Figure 2 shows the thermoelectric power of the different compositions studied as a function of the temperature. The results for $YBa_2Cu_3O_{7-\delta}$ shown in detail in Fig. 3 are similar to the measurements previously reported by other groups[16] but with values about 50% smaller. The small value observed at room temperature, $\sim 2\ \mu V\,K^{-1}$, is typical of the good metals. However, our results are significantly different from many other types of behavior recently reported by several other groups for thermopower in $YBa_2Cu_3O_{7-\delta}$, where negative values,[17,18] small positive temperature-independent values ($\sim 4\ \mu V\,K^{-1}$)[19] or larger ones ($\sim 25\ \mu V\,K^{-1}$) with negative $dS/dT$,[20] have been equally attributed to the same material.

Measurements performed in our laboratory on $YBa_2Cu_3O_{7-\delta}$ samples with different thermal treatments, show that such differences are accounted for by the large sensitivity of thermopower to the oxygen content. Single-phase samples with perfect 1:2:3 stoichiometry and submitted to a long annealing at low temperatures in pure oxygen, always showed the small values reported here, while larger values, with a behavior similar to the one reported by other authors, were found in samples not so well annealed or not so perfectly reacted.
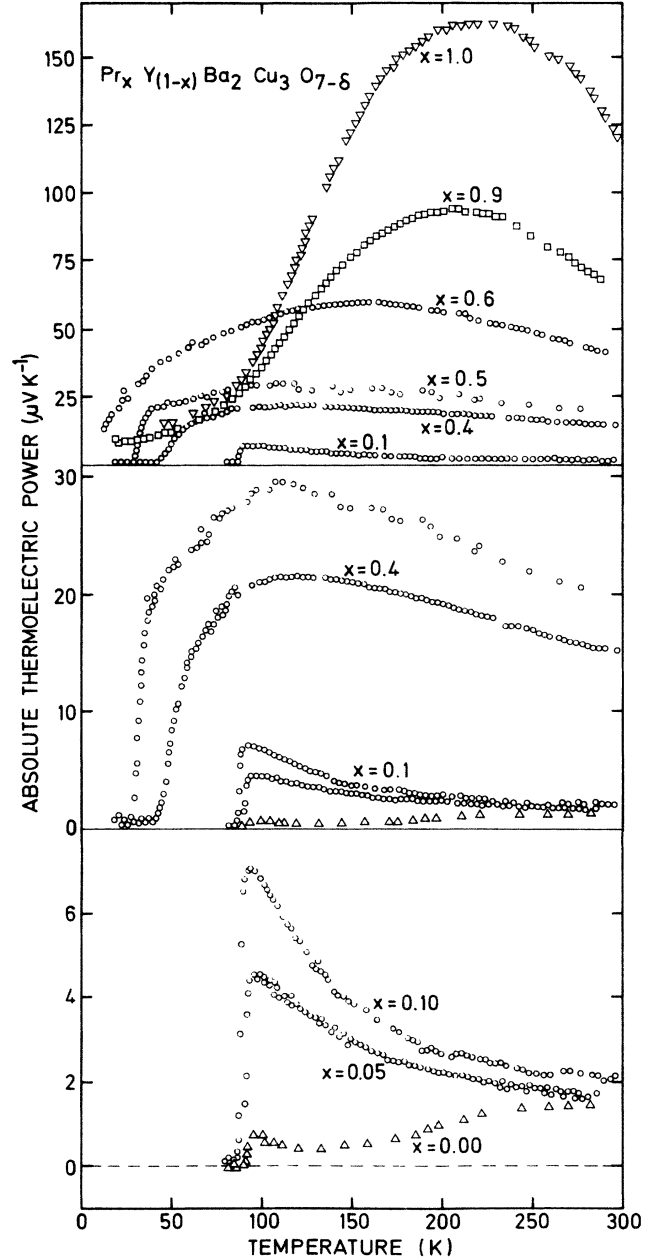


FIG. 2. Absolute thermoelectric power of $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ ($0 \leq x \leq 1$) as a function of temperature.

Neglecting correlation and possible effects deriving from electron-phonon interactions (phonon drag), the thermoelectric power $S$ in a metal (the diffusion contribution) is given by Mott's formula[21]

$$S = \frac{\pi^2 k_B^2 T}{3|e|}[d\ln\sigma(\varepsilon)/d\varepsilon]_{\varepsilon=\varepsilon_F}.\tag{1}$$

The sign of $S$ indicates the sign of the majority carriers and his magnitude is proportional to the density of states at the Fermi level $D(\varepsilon_F)$. According to this model, $S$ is expected to decrease almost linearly with decreasing tem-
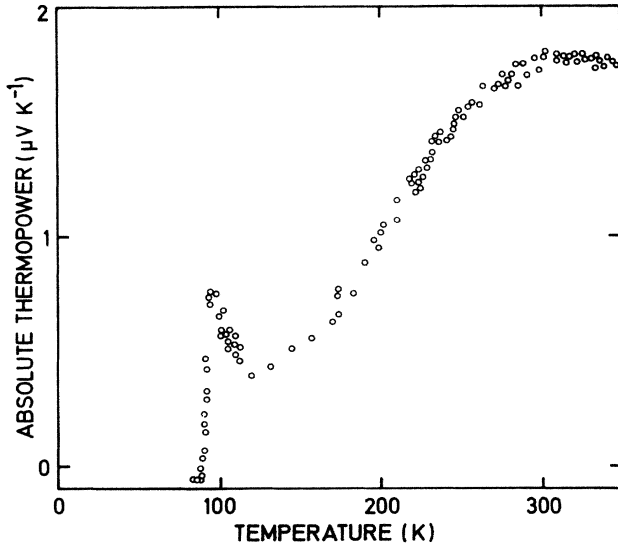
FIG. 3. Absolute thermoelectric power for $YBa_2Cu_3O_{7-\delta}$ as a function of temperature.

perature. The room-temperature values that we found for $YBa_2Cu_3O_{7-\delta}$ are of the same order of magnitude of those observed in good metals like Cu or Au, and the low-temperature deviations from this model, observed as an increase below 150 K until the superconducting transition, have been tentatively ascribed by many authors to phonon-drag effects denoting strong electron-phonon interactions in these materials.[16-20] As it will become evident by the following discussion, such interpretation is not adequate to fully explain the results, namely the temperature-independent values observed in the range 280–350 K and the effects of substitution of Pr reported in this paper.

The substitution of Pr for Y, even in amounts as small as 5%, has drastic effects on both the magnitude and the temperature dependence of the thermopower, that increases and presents a negative slope $dS/dt$. The maximum value of thermopower is observed above the superconductivity transition and is broadened with increasing $x$. As expected for a superconductor, in all compositions up to $x = 0.5$, thermopower becomes zero at a temperature in good agreement with the superconducting transition observed in resistivity. The increasing values of thermopower on cooling contrast with the metallic behavior of resistivity. In fact, the same simple model that predicts the behavior described by Eq. (1) for uncorrelated electrons in a metal, also predicts, in the case of a semiconductor or a material having a mobility gap at the Fermi level, a temperature dependence of thermopower similar to[22]

$$S = \frac{k_B}{|e|}\left[\frac{\Delta}{T} + B\right] , \tag{2}$$

where $\Delta$ is the effective gap and $B$ accounts for kinetic effects and is almost temperature independent. That is, according to the uncorrelated electron models, the present results for $0.05 \le x \le 0.5$ should be interpreted as an indication of a semiconductor or a material having localiza-

tion of states around the Fermi level, in clear contradiction to the temperature dependence of the resistivity, that is, indicative of a metal.

This type of paradox is also present for $x \ge 0.6$. In this composition range, the thermopower becomes less temperature dependent above 100 K and at lower temperatures starts approaching zero in a clear indication that conduction takes place in a continuum of states around the Fermi level, but in contrast with the activated behavior of resistivity observed in this temperature range. As advanced earlier, this activated conductivity in this case can be attributed either to the interparticle contacts or to transport by hopping between localized states. The apparent disagreement between the temperature dependence of the resistivity and the thermopower is a general feature in this oxide, and it clearly demonstrates that the electrical properties of these ceramics cannot be described within the simple uncorrelated electronic picture currently adopted for wide band materials. In addition, it strongly supports the recently proposed superconducting mechanisms based on the Hubbard model.[23]

The almost temperature-independent behavior of thermopower observed for $x \ge 0.4$ and temperature higher than 100 K, to the best of our knowledge, can only be understood within the picture of correlated electrons in a narrow band. In the high-temperature limit ($k_B T$ larger than the bandwidth) of a narrow-band material, the thermopower is dominated by the entropy of distribution of the charge carriers among the available sites. The kinetic energy contribution is negligible, and in the case of large on-site Coulomb correlations ($U$), it is given by the Heikes formula[24] generalized by Chaikin, Beni, and Kwak:[25,26]

$$S = -\frac{k_B}{|e|}\ln\left[\frac{1-\rho}{\rho}\right] - \frac{k_B}{|e|}\ln 2 , \tag{3}$$

where $\rho$ is the number of carriers per site and the second term accounts for the spin entropy of the carriers. In these compounds, the conduction band has a strong $d$ character,[8-10] the conduction involving hopping of electrons from $Cu^{2+}$ ($d^9$) to $Cu^{3+}$ ($d^8$), and $\rho$ is given by the ratio of $Cu^{2+}$ ions to the total number of sites. It is well known from the chemistry of praseodymium that this atom has a stable 4+ oxidation state as opposed to Y where the more stable oxidation state is 3+. Thus, the substitution of Pr for Y, keeping constant all structural factors, primarily increases the band filling and $\rho$ decreases with increasing $x$. In this case, we cannot establish a simple and precise relation between $\rho$ and $x$ because in the structure, there are actually two types of Cu atoms that lead to different partially filled bands.[8-10] In the case that all Cu atoms can be considered equivalent, we have $\rho = \frac{1}{3}(2 + x + 2\delta)$. It should be noted that in the case of magnetic ordering, the term corresponding to the spin entropy will be absent or depressed. Also, an extra similar term should be considered to take into account the possible orbital twofold degeneracy of the carriers as it happens, if they are in $d$ levels of $Cu^{2+}$ atoms in an octahedral site.

In any case, this model predicts a temperature-

independent thermopower, and qualitatively describes well the observed increase of thermopower with $x$. The same model also predicts a similar dependence of thermopower on the oxygen content ($\delta$), and therefore can explain, in a similar way, the different results reported by several authors for $YBa_2Cu_3O_{7-\delta}$. Although the decrease of the oxygen content ($\delta$) has a similar effect to the increase of $x$, the substitution with Pr seems to us to be the only way of making a significant excursion on the band filling without change in the crystal structure and without disturbing the Cu—O chains.

In addition to the increasing band-filling effect associated with this substitution, there are also disorder effects to be considered, but in view of the fact that the rare-earth position is separated from the Cu—O planes and chains involved in the conduction processes, these are expected to be of minor importance to the transport properties. The disorder effects are stronger for $x = 0.5$ and they can probably induce some carrier localization responsible for the negative $d\rho/dT$ observed just above $T_c$. A similar upturn of resistivity before the superconducting resistance drop is also present in other oxides containing substitutional disorder, and therefore, is most unlikely due to disorder-induced localization.

The decrease of thermopower approaching zero on cooling below $\sim 100$ K, as observed for $x \geq 0.6$, is indicative of conduction via a continuum of states around the Fermi level, as expected in a partially filled band. Such behavior is also qualitatively predicted by models of correlated electrons in partially filled narrow bands in the region of temperature where $k_B T$ becomes smaller than the bandwidth,[25] or in the case of intermediate on-site Coulomb repulsions $(U \sim 4t)$.[27]

Finally, we can summarize our results in Fig. 4 by representing the phase diagram of $Pr_x Y_{1-x} Ba_2 Cu_3 O_{7-\delta}$ $(0 \leq x \leq 1)$. For $x$ up to 0.55, there is a superconducting transition temperature measured in good agreement with both the resistivity and the thermopower. The decrease of the superconducting transition temperature with increasing $x$ is probably a consequence of both the decrease of the orthorhombic distortion and the displacement of the Fermi level to regions of lower density of states, in agree-
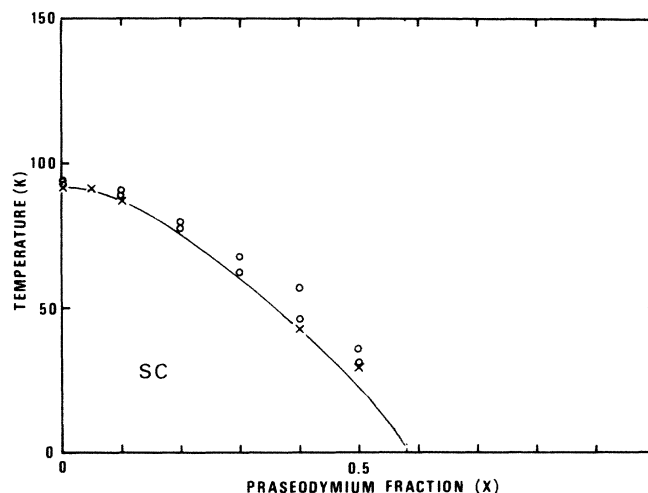


FIG. 4. Phase diagram for $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ ($0 \leq x \leq 1$). O, temperatures for 90% and 10% resistance drop. ×, zero thermopower temperature. The solid line is a guide to the eye separating the superconducting state (SC).

ment with band-structure calculations.[10,11,28] For $x \geq 0.55$ the superconductivity is lost in spite of the presence of an orthorhombic structure.

In conclusion, the present results on $Y_{1-x}Pr_xBa_2$-$Cu_3O_{7-\delta}$ $(0 \leq x \leq 1)$ show that the substitution of Pr for Y progressively decreases the superconducting transition temperature (which is no longer existent for $x \gtrsim 0.55$). This effect is basically due to the increase of the band filling with increasing $x$. The thermoelectric power increases significantly with increasing $x$, and together with resistivity data shows that the electronic properties of these oxides are dominated by electron correlation effects in narrow bands.

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