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# Resistivity and thermoelectric-power measurements of $Pr_xY_{1-x}Ba_2Cu_3O_{7-\delta}$ up to 1200 K and an electronic-structure analysis

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We report measurements of absolute thermoelectric power and resistivity in $Pr_xY_{1-x}Ba_2Cu_3O_{7-\delta}$, as function of $x$ and $\delta$, over a wide temperature range. At high temperature, the substitution of Pr for Y does not affect the thermopower and resistivity; Pr behaves then as a trivalent ion: $Pr^{3+}$. For small $x$ and $\delta$ the effects of substitution of Y by Pr and of oxygen deficiency on the low-temperature resistivity are additive. A simple electronic-structure model is proposed to account for thermopower as function of temperature, $x$, and $\delta$.

## I. INTRODUCTION

The evolution of the properties of the $Pr_xY_{1-x}Ba_2Cu_3O_{7-\delta}$ (Pr-Y-Ba-Cu-O) system, as function of $x$, in its normal and superconducting states has been widely studied, in the expectation that it will provide important clues about the electron states, excitations, and interactions in the 1:2:3 compounds. The great interest in this subject stems from the observation that $PrBa_2Cu_3O_7$ (Pr-Ba-Cu-O) is the only rare-earth 1:2:3 compound which is nonsuperconducting in the orthorhombic, fully oxygenated form. The experimental results and the mechanisms proposed for the quenching of superconductivity in Pr-Y-Ba-Cu-O are reviewed in a series of recent papers (see Refs. 1–6, and references quoted therein).

We addressed the problem of the evolution with increasing $x$ of the electronic structure of Pr-Y-Ba-Cu-O in its normal state and, especially, the question of the carrier concentration in the conduction band of this system. The similarity between the changes in the electronic properties, e.g., resistivity ($\rho$) in the normal state, changes in the superconductivity transition temperature ($T_c$) due to increase in the Pr content $x$, and the changes due to the reduction of the oxygen content in $YBa_2Cu_3O_{7-\delta}$ (Y-Ba-Cu-O), leads to the conclusion that the valency of Pr in Pr-Y-Ba-Cu-O is higher than 3 (up to 4). The additional electrons, contributed by $Pr^{4+}$ ions, apparently fill holes (empty electron states) in the conduction band. This, therefore, resembles the effect of adding electrons into this band, when oxygen atoms of the chains are removed from the lattice. However, other experiments, e.g., x-ray photoemission spectroscopy,[7] x-ray absorption spectroscopy,[8,9] and also some band calculations,[3] indicate that the valency of Pr in Pr-Y-Ba-Cu-O remains 3+.

Our work on the transport properties of Y-Ba-Cu-O at high temperatures led us to this subject. Such experiments proved to be a powerful tool in the study of the electronic structure of Y-Ba-Cu-O.[10–12] We were particularly interested in the reversal of the sign of the absolute thermopower ($S$), observed at high temperature ($T$) under low oxygen pressure [$P(O_2)$]. We tried to push the sign change of $S$ to lower temperature by reducing the partial pressure of oxygen, but it seemed that a more efficient method to fill the holes in the conduction band of Y-Ba-Cu-O would be by appropriate substitution. At that time Pr, believed to be tetravalent, seemed to be the best candidate.

The experimental results presented below show that the effect of Pr on the properties of Pr-Y-Ba-Cu-O, in its normal state, diminishes with increasing temperature. At 1000 K the transport properties of Pr-Y-Ba-Cu-O closely resemble those of Y-Ba-Cu-O; hence the effective valency of Pr seems to be very close to 3+ at high temperatures. This result explains why, unlike Ce and Tb, Pr forms the 1:2:3 structure, as $Pr^{3+}$ stabilizes it at high temperature. We expect that a detailed study of the temperature dependence of the transport properties of Pr-Y-Ba-Cu-O will help in understanding why at low temperatures it behaves so differently from the other rare-earth 1:2:3 compounds.

## II. EXPERIMENT

Ceramic samples of Pr-Y-Ba-Cu-O were prepared by the standard procedure,[2,6] special care being taken to ensure their homogeneity, which was checked by x-ray powder diffraction. Three types of samples were prepared for each composition: pellets for gravimetric measurements, pellets with embedded gold wire contacts for resistivity measurements at low temperatures, and long bars with embedded gold wires for simultaneous measurements of resistance and thermopower at high temperatures. The pellets were formed by uniaxial compression and the bars in an isostatic press. The embedding of wires in the samples prior to sintering offers a significant advantage: These contacts remain very stable both during prolonged measuring runs at high temperatures and also after repeated annealing at various temperatures and oxygen pressures.

In each case equilibrium was established by monitoring the time dependence of the sample resistance following a change of the external conditions. Below about 600 °C, the time constant for equilibration was of the order of days. Hence measurements under equilibrium conditions were carried out above this temperature (apart from a few selected cases where the samples were equilibrated at lower temperatures). The starting point for each Pr-Y-Ba-Cu-O sample was at ~450 °C under $P(O_2)=1$ bar, where the samples were kept for 1–2 weeks in order to reach the limiting oxygen content $\delta=0$, as closely as possible.

Above room temperature we carried out two types of measurements.

(1) "Slow measurements" at temperatures above 550–600 °C, under equilibrium conditions [$P(O_2)=1$ or 0.01 bar]. The oxygen content of the samples was determined by the ambient temperature and oxygen pressure, using the available phase diagrams for Y-Ba-Cu-O (Ref. 13) and Pr-Ba-Cu-O.[14] Within the temperature and pressure range where we worked, there is a small difference between the two sets of graphs, and for samples of intermediate composition we interpolated between the two sets of data.

(2) "Fast measurements" below ~550 °C, where the measurements were carried out as quickly as possible, in order to preserve the frozen-in oxygen content. Between 400 and 500 °C the kinetics of oxidation-reduction are too slow for the bulk of the large specimens to reach equilibrium, but fast enough to change the stoichiometry of a thin surface layer of the sample during cooling or heating at finite rate, as required by the measurements. Such a thin layer, which may be unnoticed in, say, gravimetric measurements, can be crucial in transport experiments. Measurements performed between room temperature and ~400 °C give reasonably reproducible results.

(3) For low-temperature measurements ($T<$ 300 K), sets of samples with and without contacts were equilibrated together and quenched to room temperature. Changes in oxygen stoichiometry of the samples were determined from the weight loss of the accompanying contactless samples. We estimated that gravimetric measurements correspond to determination of changes of $\delta$ to better than $\pm0.01$. However, minor inhomogeneities or foreign phases, which might have been introduced during quenching, could not be detected by x-ray diffraction, as its limit of detection was about 5%. The agreement with the values of $\delta$ determined from phase diagrams was within 0.05. Hence all our values of $\delta$ for quenched samples are nominal.

## III. EXPERIMENTAL RESULTS

### A. High temperatures

As stated in the Introduction, we were trying to push the sign reversal observed in oxygen-deficient Y-Ba-Cu-O to lower temperature, assuming Pr to be a tetravalent ion. We started with $x=0.2$ and 0.4. As we did not obtain the anticipated effect for these concentrations, we went directly to $x=1$. Below we present the results for these concentrations and for $x=0$ (taken from Refs. 10–12).

In Figs. 1 and 2 we plotted the temperature dependence of the resistivity and of the absolute thermopower for samples under $P(O_2)=1$ and 0.01 bar, respectively. Note the different temperature ranges of measurements of the "slow" (equilibrium conditions) and of the "fast" (frozen-in oxygen compositions) measurements. We also include some of the data obtained by other laboratories.[6,15]

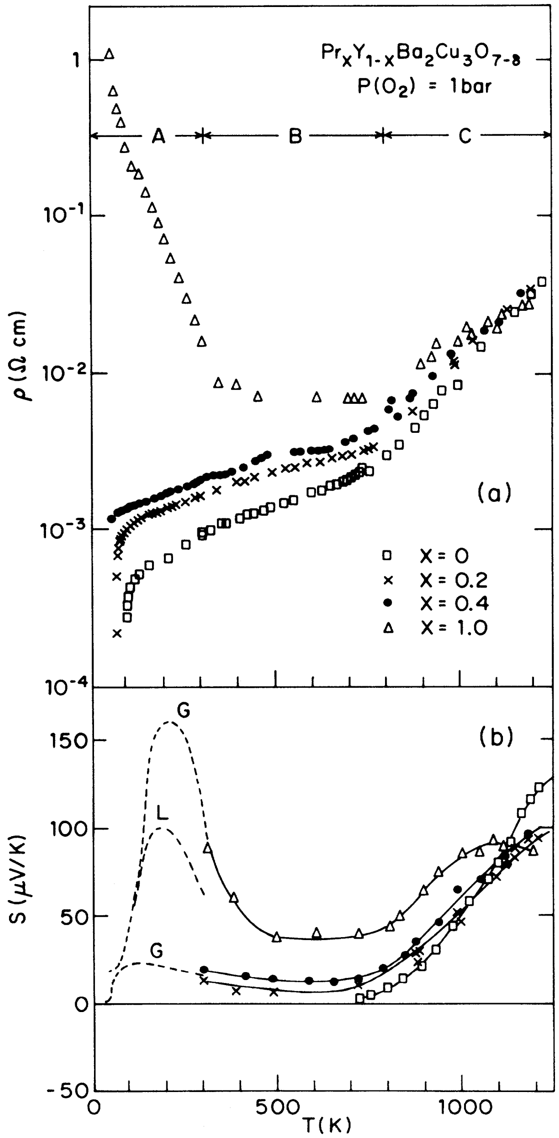

FIG. 1. Thermopower $S$ and resistivity $\rho$ of $Pr_xY_{1-x}Ba_2Cu_3O_{7-\delta}$ as function of temperature under $P(O_2)=1$ bar. In region C, measurements under equilibrium conditions. In region B, "fast measurements" (see text). In region A, data taken from literature; $G$, from Ref. 15; $L$, from Ref. 6.

A remarkable result is that the variations of the Pr content hardly affect the high-temperature transport properties of Pr-Y-Ba-Cu-O, in contrast to the dramatic changes that occur at low temperatures. In Fig. 1, above 1150 K, the curves for all samples with different Pr content converge, and while the graph for $\rho(x=1)$ rises slower than for $\rho(x=0)$, the spread of the values of $\rho$ for all samples is within a factor of 1.5. For $S(x=1)$ there is an indication of a shallow maximum at high temperatures, around 1100 K.

"Fast measurements" at $P(O_2)=0.01$ bar show trends similar to those obtained under $P(O_2)=1$ bar. The differences in the absolute values of $\rho$ and $S$ are due to changes in oxygen stoichiometry.[13,14] For $x<1$, $d\rho/dT>0$ and $S(T)$ exhibit plateaux. For $x=0.2$ and 0.4, $d\rho/dT$ becomes negative only below room temperature. For $x=1$ the plateaux regime of $S$ shrinks to a dip between 500 and 800 K with $S\cong110$ $\mu$V/K. The absolute magnitude of $d\rho/dT$ decreases with increasing temperature, but its sign remains negative. From the phase diagram[14] and from $S$, we estimate that for Pr-Ba-Cu-O, under these conditions, $\delta\sim0.50$. We also include measurements of $S(T)$ below room temperature for samples of Pr-Ba-Cu-O with similar values of $\delta$, as reported by the IBM group.[6] The two sets of curves join reasonably well at 300 K.

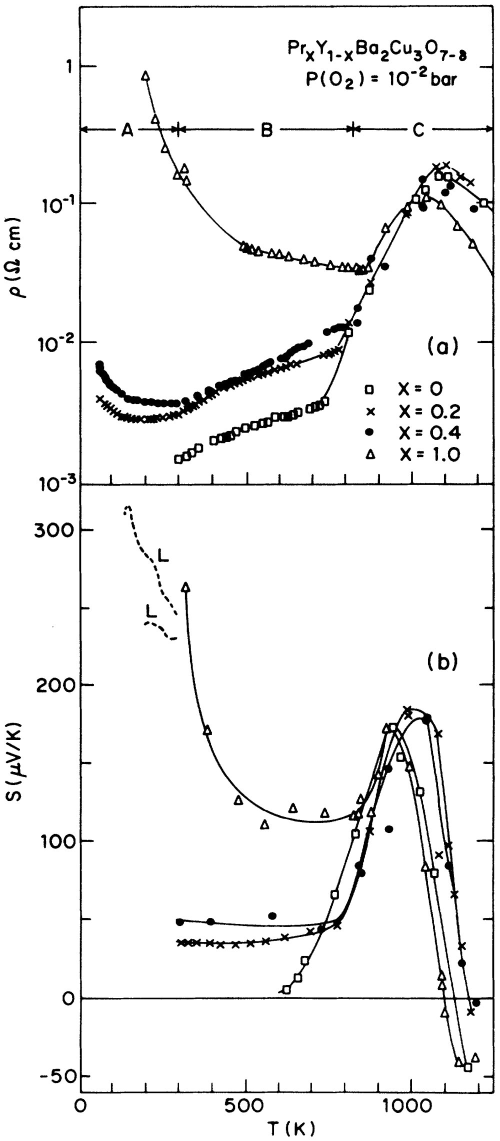

FIG. 2. $S$ and $\rho$ of $Pr_xY_{1-x}Ba_2Cu_3O_{7-\delta}$ as function of temperature under $P(O_2)=0.01$ bar. In region C, measurements under equilibrium conditions. In region B, "fast measurements" (see text). In region A: $L$, data taken from Ref. 6.

### B. Low temperatures

So far, below room temperature we have measured only $\rho(T)$. In this regime we found a very rich variety of behavior. We present separately the cases of low and high resistivity. In the cases where the maximum value of $\rho$ does not exceed $10^{-2}$ $\Omega$ cm, $\rho$ was plotted versus $T$ on a linear scale (Fig. 3), while for $\rho\geq10^{-2}$ $\Omega$ cm plots of $\log\rho$ versus $1/T$ seemed more appropriate (Fig. 4).

Curves for ($x=0.2$, $\delta\sim0$) and for ($x=0.4$, $\delta\sim0$), shown in Fig. 3, are similar to the corresponding plots in Ref. 15. Here $T_c$ drops with $x$, while the normal-state resistivity increases with $T$ and $x$. Note that the curve for ($x=0.4$, $\delta=0$), is, over most of the temperature range, midway between the curve for ($x=0.2$, $\delta\sim0$) and that for ($x=0.2$, $\delta=0.4$), suggesting that, in this limited range of $(T,x,\delta)$, $\rho$ is a function of $T$ and of a single parameter: $q=(x+\delta)$.

For ($x=0.2$, $\delta=0.4$), $d\rho/dT$ becomes negative below $\sim150$ K. This resembles the behavior seen in Fig. 1 of Ref. 15 for ($x=0.6$, $\delta\sim0$). Below 150 K, both $\rho$ and $|d\rho/dT|$ increase appreciably for small increases in $q$ (see the upper two curves in Fig. 3). The upper curve of Fig. 3 [for ($x=0.4$, $\delta=0.47$)] exhibits at $T\sim60$ K an unusual

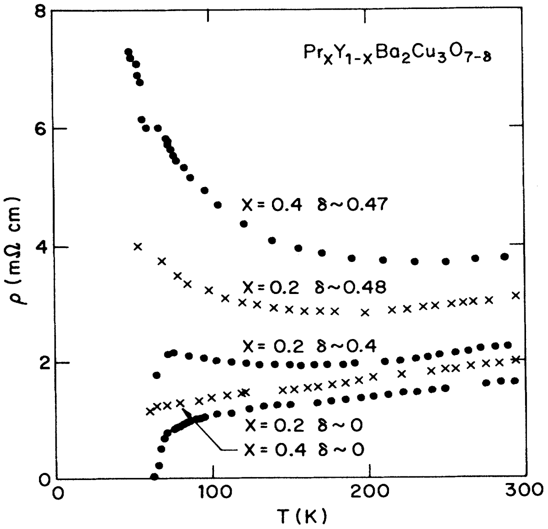

FIG. 3. Resistivity of $Pr_xY_{1-x}Ba_2Cu_3O_{7-\delta}$ as function of temperature.

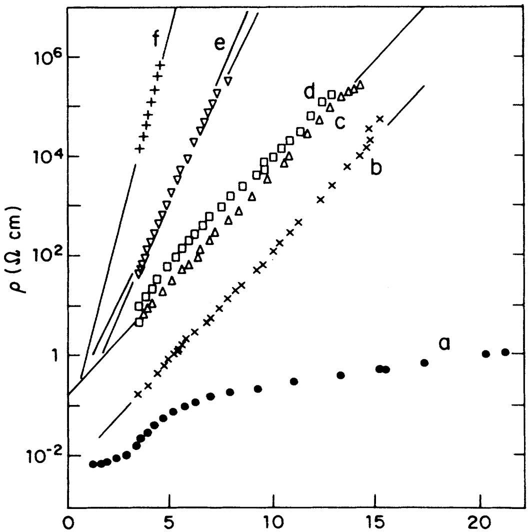

FIG. 4. Semilog plot of $\rho$ vs $1/T$ for $Pr_xY_{1-x}Ba_2Cu_3O_{7-\delta}$. The Pr and the (nominal) oxygen content for each of the graphs $a$–$f$ is given in Table I.

step in the $\rho(T)$ graph. We repeated the measurements several times, on two different samples prepared under the same conditions, and the results were perfectly reproducible. This may indicate a phase transition, presumably the Néel point of this composition.

In cases of large $\rho$ (and $|d\rho/dT|$) $\log\rho$ was plotted versus $1/T$ (Fig. 4), and the results are summarized in Table I. Additional runs were not included in Fig. 4, so as not to overcrowd the drawing. In most cases the observed behavior may be interpreted as temperature-activated transport. For large $\delta$ the material is a semiconductor, with a single activation energy—see, for example, graphs $b$, $c$, and $f$ in Fig. 4. In other cases two distinct slopes, below and above $T_b$, could be distinguished in the $1/T$ graph [e.g., curve $e$ and run $g$ (not shown)]. More complicated is case $d$, which shows slight curvature in the plot, but lies closely to the fairly straight line of sample $c$. The latter is straight over 4 orders of magnitude of $\rho$. (It should be noted that case $d$ is pure Y-Ba-Cu-O, while $c$ is pure Pr-Ba-Cu-O).

In still more complicated cases (e.g., graph $a$ and sample $h$ of Table I), the curves deviate strongly from straight lines. Such behavior in Pr-Ba-Cu-O ($x=1$, $\delta=0$) has been already reported in Refs. 6 and 16, who concluded that it cannot be interpreted in terms of a single temperature-activated mechanism. It is possible that the conductivity here is via variable-range hopping (VRH).[17]

The effect of oxygen content in Pr-Ba-Cu-O can be seen in a sequence of runs, on one sample shown by curves $a$, $b$, $c$ and $f$ in Fig. 4. Initially, the sample was fully oxygenated as described in Sec. II. We assumed that its initial composition was $PrBa_2Cu_3O_7$ (i.e., $x=1$, $\delta=0$), and its low-temperature resistivity is shown as $a$ in Fig. 4. The sample was then heat treated at $P(O_2)=0.01$ bar and $T=600\,^\circ C$ and quenched. The weight loss gave its composition as ($x=1$, $\delta=0.4$), in agreement with Ref. 14; its resistivity is shown as $b$ in Fig. 4. The graph is a straight line over more than 5 orders of magnitude of $\rho$. The oxygen content was further reduced by heat treatment at $P(O_2)=0.01$ bar, $T=900$ K, and quenched, giving ($x=1$, $\delta=0.92$)—curve $c$. As the slope of the resistivity graph remained unchanged (cf. $b$ and $c$), we suspected that during quenching a thin surface layer was reoxidized and that this accounted for the unchanged slope (although the resistivity of the sample increased). We therefore repeated the heat treatment (adding also a Y-Ba-Cu-O sample for comparison measurements), but this time, just before quenching, connected the furnace to a (rotory) vacuum pump. This run provided two curves: $f$ ($x=1$, $\delta=1.02$) and $d$ ($x=0$, $\delta=0.98$). [By comparing the phase diagrams of Y-Ba-Cu-O (Ref. 13) and of Pr-Ba-Cu-O,[14] we expected that, on the contrary, the oxygen deficiency in $f$ would be smaller than in $d$ (assuming that in both cases the starting material was $\delta=0$).]

To sum up, in $PrBa_2Cu_3O_{7-\delta}$, as the oxygen deficit $\delta$ increases, the activation energy increases. There is no clear answer, whether the conduction takes place through excited states above the band, at constant activation energy, or by hopping between "localized" states. In cases where there is a gradual change of slope of the $\log\rho$ against $1/T$ graph (and hence gradual change of activation energy), as in case $a$ ($x=1$, $\delta\sim0$), it is possible that the conduction is via VRH or an even more complicated

TABLE I. Characterization and results of the Pr-Y-Ba-Cu-O samples on which "low-temperature" resistivity measurements have been carried out. $x$ and $\delta$ indicate the Pr and O contents, respectively (see text). $E_H$ and $E_L$ are activation energies taken from the $\log\rho$-vs-$1/T$ graphs above and below $T_b$, respectively. The results of runs $a$–$f$ are shown in Fig. 4.

| Run | $x$ | $\delta$ | $E_H/k$ | $E_L/k$ | $T_b$ |
|---|---|---|---|---|---|
| $a$ | 1.0 | ~0 | VRH(?) | | |
| $b$ | 1.0 | 0.40 | ~1000 K | | |
| $c$ | 1.0 | 0.92 | 1000 K | | |
| $d$ | 0.0 | 0.98 | VRH(?) | | |
| $e$ | 0.2 | 0.82 | 2400 K | 1600 K | 170 K |
| $f$ | 1.0 | 1.02 | ~4000 K | | |
| $g$ | 0.0 | 0.62 | 1000 K | 700 K | 130 K |
| $h$ | 0.4 | 0.86 | VRH(?) | | |

case of a transition from next-neighbor hopping to VRH. Further experiments on this problem are in progress.

## IV. INTERPRETATION

In the past we interpreted successfully the normal-state transport properties of orthorhombic Y-Ba-Cu-O in terms of the "narrow-band" model.[10-12] Here we will attempt to adapt this model to Pr-Y-Ba-Cu-O and to account for the effect of substitution of Y by Pr. This model assumed a narrow conduction band (CB) of width $W$, with two states per formula unit containing $n$ effectively noninteracting electrons (consistent with a Fermi-liquid behavior). In Ref. 11 it was shown that in pure Y-Ba-Cu-O $n=1+\delta$, that is, the $(1-\delta)$ chain oxygen atoms create $(1-\delta)$ holes in the CB. This narrow-band model predicts that for constant band filling, at sufficiently high temperatures ($T > W/4k$, where $k$ is the Boltzmann constant),[18] $S$ becomes independent of temperature, with $S$ given by

$$S=(k/e)\ln[n/(2-n)] , \tag{1}$$

$k/e=86\ \mu\mathrm{V/K}$, and $n$ is the number of CB electrons per unit cell.

In Pr-Y-Ba-Cu-O we find that at high temperature ($T > 1000$ K), for samples with different Pr content, the graphs of $\rho$ and $S$ overlap, that $\rho$ and $S$ become independent of the Pr content $x$, and are functions only of the oxygen content and temperature. Thus, at high temperature, Pr behaves like the trivalent ion $Y^{3+}$. However, as the temperature decreases, the presence of Pr manifests itself more and more strongly. At constant oxygen content (regime B), there appears a plateau. This tendency toward saturation of $S(T)$ is observed for all curves in Figs. 1 and 2 in regime B (constant composition region), which justifies the use of Eq. (1) for $0 \le x \le 1$. At $P(O_2)=1$ bar, around 600 K, one obtains $S \sim 0$ for $x=0$, and $S \sim 40\ \mu\mathrm{V/K}$ for $x=1$. Using Eq. (1) in the last case, one gets $n=1$ for Y-Ba-Cu-O and $n=1.23$ for Pr-Ba-Cu-O. Thus, in Pr-Ba-Cu-O ($x=1$) at $T \sim 600$ K and $\delta \sim 0$, only 0.23 additional holes in the CB have been filled, over and above the band filling in Y-Ba-Cu-O. Hence, at least at these temperatures, the effective valency of Pr is apparently closer to 3 than 4. The same conclusion can be drawn also from the graphs for $x=0.2$ and 0.4 in Fig. 1. The apparent insensitivity of transport properties to changes of Pr content is therefore surprising. It underlines the equivalence of Pr and Y at elevated temperatures.

As the temperature decreases further, $S$ start to increase, which suggests that there is transfer of electrons into the conduction band, presumably from the Pr ion states and hence formation of $Pr^{4+}$ ions.

The proposed generalization of the narrow-band model to account for the complex dependence of $S$ in Pr-Y-Ba-Cu-O as function of composition and temperature is rather schematic, but at this stage more elaborate models do not seem warranted, as the available experimental data are limited. We will try to justify our assumptions.

In Pr-Y-Ba-Cu-O the thermopower $S$ shows a maximum below $\sim 220$ K, where both the temperature of the maximum and its magnitude increase with $x$. In the proposed model this effect is connected with transfer of electrons between the $4f$ states of the Pr atom and the conduction band as function of temperature. By judicious choice of parameters, such a model can be made to simulate closely the experimental results of $S$ for $0 \le x \le 1$ and $\delta < \frac{2}{3}$. However, these changes of population cannot account alone for the very high, seemingly temperature-activated, resistivity in Pr-rich samples at low temperatures. Apparently, as the Pr content increases, it affects not only the population of the CB, but also the transport mechanism of electrons.

In our model for Pr-Y-Ba-Cu-O we additionally assume that the Pr $f$-electron energy levels overlap the CB, but the CB and $f$ states do not interact or hybridize, and both retain their identity. This assumption is plausible because, as a result of spatial separation and electron correlations, Pr($4f$) orbitals tend not to hybridize with CB orbitals, maintaining their atomic character. As a consequence, electrons are transferred between the CB and Pr($4f$) states, as determined by the chemical potential ($\mu$) and temperature. We assume further that the CB and $f$ levels of $Pr^{3+}$ are isolated from other bands or levels so that $\mu$ is determined solely by the populations of the above two types of states.

The possible ionic states of a Pr atom in Pr-Y-Ba-Cu-O are either 4+ (with one $f$ electron) or 3+ (with two $f$ electrons). Under standard statistics of localized levels in thermal equilibrium (see, e.g., Eq. 28.30 in Ref. 19), we get the mean number of $4f$ electrons per Pr atom as

$$\langle n_f \rangle = \frac{\sum_i \exp[-\beta(E_i-\mu)] + 2\sum_j \exp[-\beta(E_j-2\mu)]}{\sum_i \exp[-\beta(E_i-\mu)] + \sum_j \exp[-\beta(E_j-2\mu)]} , \tag{2}$$

where $E_i$ and $E_j$ are the energies of singly or doubly occupied Pr($4f$) states, respectively, and $\beta=1/kT$. The mean fractional population of $Pr^{4+}$ ions is

$$\langle n(Pr^{4+}) \rangle / n(Pr) = 2 - \langle n_f \rangle = [1 + a\exp(\beta\mu)]^{-1} ,$$

where

$$a = \frac{\sum_j \exp[-\beta(E_j-\mu)]}{\sum_i \exp[-\beta(E_i-\mu)]} .$$

Here, again the $i$th index refers to energy levels of $Pr^{4+}$ and the $j$th to those of $Pr^{3+}$. As the electron-level scheme of Pr in Pr-Y-Ba-Cu-O is not known in detail, we consider here only a single $Pr^{4+}$ level, $E_1$, of multiplicity $g_1$, and a corresponding one of $Pr^{3+}$, $E_2$, of multiplicity $g_2$. One obtains $a=g\exp(-\beta E_0)$, where $g=g_2/g_1$ and $E_0=E_2-E_1$.

The condition for neutrality (for small $\delta$) is

$$n = 1 + \delta + x/[1 + a\exp(\beta\mu)] , \tag{3}$$

where $n$ is the number of electrons in the CB per formula unit. The conductivity ($\sigma$) and the absolute thermopower are calculated from standard relations:[17]

$$\sigma = -\int \sigma(E,T)(df/dE)dE \ , \tag{4a}$$

$$S = \frac{\int (E-\mu)\sigma(E,T)(df/dE)dE}{\sigma} \ . \tag{4b}$$

For simplicity we assume a box-shaped function for $\sigma(E)$, independent of temperature (see inset in Fig. 5). Other, more realistic choices for $\sigma(E)$ change the numerical values obtained, but the general shape of the resulting curves is not greatly affected. In Fig. 5 we plotted the thermopower $S$, for several values of $x$ and $\delta$.

The adjustable parameters are $E_0$ and $g$. As can be seen in Figs. 1 and 2, at high temperatures ($T > 400$ K), at constant oxygen content (region B), $S$ becomes temperature independent. It can be shown that in the model proposed, at $kT/W > \sim 0.5$, the exponential term in Eqs. (4a) and (4b) reaches an almost constant value. In order to obtain these experimental "high-temperature" saturation values of $S$, we found that the parameter $g$ must be about 6, which implies that in the relevant energy range there are many more two-electron states than single-electron states. We chose $E_0$ at the top edge of the conduction band (see Fig. 5) in order to fit $S_{\max}$ for $x=0.4$. This value fits well all measurements of $S(T)$, for $x < 0.6$, both ours and from Ref. 15.

According to this model, the resistivity will remain "metallic." The substitution of Pr will affect the density of carriers, but this is only a small effect as far as $\rho$ is concerned. Scattering due to Pr ions and disorder due to coexistence of $Pr^{3+}$ and $Pr^{4+}$ ions might affect the transport mechanisms and cause Anderson localization. The narrow CB in our model is probably a coherent many-body effect, which is disrupted by the Pr level, resulting in a decrease in mobility [namely, in $\sigma(E,T)$]. Since, in Eq. (4b), $\sigma(E,T)$ appears in both the numerator and denominator, $S$ is not affected greatly by such a decrease, but $\rho$ is.

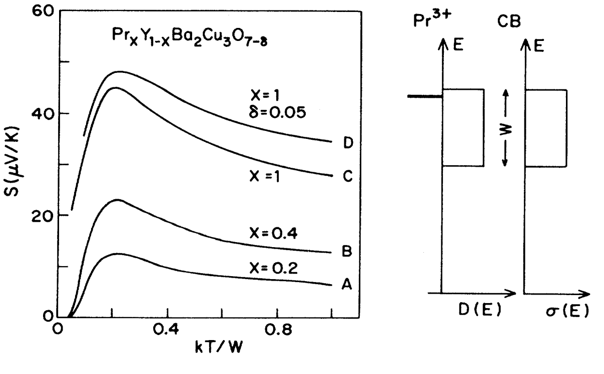

FIG. 5. Calculated thermopower $S$, as function of $kT/W$, for a model, consisting of a narrow band with constant density of states $D(E)$, constant conductivity function $\sigma(E)$, and of $Pr^{3+}$ ionic level (see right half of the figure). Parameters used are $g=6$, $\delta=0$ except for curve $D$, where $\delta=0.05$, with $E_0$ at the top edge of the conduction band.

The initial rise of $S(T)$ is normal for transport in a more-than-half-filled band at $T \ll W/k$. Were the band filling to stay constant at all temperatures, $S$ would eventually saturate at its (constant) narrow-band value. The high multiplicity ratio ($g=6$) of the $f$ level causes electron transfer to the Pr levels at the expense of the conduction band. It should be mentioned that as far as the population in the CB is concerned, the same apparent effect can be obtained either when an ion with high multiplicity of energy levels is present (as assumed above) or if the energy of the ion states decreases linearly with temperature.

For $x=1$ we found that no single choice of (temperature-independent) parameters can reproduce the experimental results. At high temperature [$T > T$(saturation)$\sim 600$ K], $E_0$ at the top edge of the conduction band and $g=6$ give the right magnitude of $S$ (Fig. 5, curve $C$); however, the high maximum at low temperatures cannot be reproduced with these parameters, and at low temperatures the calculated $S_{\max}$ is about 2–3 times smaller than the experimental results. Also, $\rho$ measurements indicate that the conduction mechanism at low temperature is very different than that in $x < 0.5$.

No doubt the electron-correlation effects have a significant role in the structure and shape of the conduction band. We suspect that also the antiferromagnetic order[4,20] for $x=1$ gives rise to additional splitting (and possibly further modification) of both the CB and Pr energy levels below room temperature. Curve $D$ (Fig. 5) shows the effect of small deviations from oxygen stoichiometry. We expect that further experiments on Pr-rich samples will help to clear up the riddle of conductivity mechanism, especially in cases where there seem to be indications of localization and VRH.

It should be pointed out that the above model neglects a number of other important effects, which may affect the conduction band, viz., additional splitting or relative shifts of the band levels, hybridization, changes in transport mechanism, etc. The above model accounts simply for the transport properties of Pr-Y-Ba-Cu-O with $x \le 0.4$. For $x=1$ we discussed here only one of several possible assumptions. However, it might not be consistent with the apparent constancy and magnitude of the paramagnetic moment of the Pr ion in Pr-Y-Ba-Cu-O, which is reported to be $M=(2.4-2.9)\mu_B$, independent of $x$ and of temperature (for $T < 300$ K).[21]

The transport properties of the semiconducting region in the phase diagram of Pr-Y-Ba-Cu-O deserve further investigation, in order to unravel the complicated effects of $x$, $\delta$, and history. In the metallic regime the transport properties of good ceramic samples present a reliable measure of the properties of the *ab* plane. It is not yet clear whether this applies also in the semiconducting regime. Therefore, it is important to carry out measurements also on single crystals and oriented thin films, especially in the semiconducting regime, in order to remove any possible effects of grain boundaries. Of special interest is the behavior of the transport properties in the vicinity of the Néel temperatures at different points within the $(x,\delta)$ phase diagram.

## V. CONCLUSIONS

(1) In $Pr_xY_{1-x}Ba_2Cu_3O_{7-\delta}$, at high temperatures, $\rho$ and $S$ are independent of the Pr content $x$ and are a function of the oxygen content *only* (i.e., at high temperatures Pr behaves like the trivalent ion $Y$).

(2) For small $x$ and $\delta$ the resistivity at low temperature is determined by a single variable $q=(x+\delta)$.

(3) The narrow-band model[10-12] can be applied to Pr-Y-Ba-Cu-O. The dependence $S(T)$ for $0\leq x\leq 0.4$ can be accounted for by a simple model consisting of a narrow conduction band and praseodymium atomic levels, independent of each other, with the $Pr^{3+}$ levels above the center of the CB.

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