

Hopping conductivity in fully oxygenated $\text{PrBa}_2\text{Cu}_3\text{O}_y$, $\text{YBa}_2\text{Cu}_2\text{CoO}_y$, and $\text{PrBa}_2\text{Cu}_2\text{CoO}_y$

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We report results of a comparative study of three nonmetals related to the 1-2-3 cuprate superconductors: fully oxygenated $\text{PrBa}_2\text{Cu}_3\text{O}_y$ (PBCO), $\text{YBa}_2\text{Cu}_2\text{CoO}_y$ (YBCCO), and $\text{PrBa}_2\text{Cu}_2\text{CoO}_y$ (PBCCO). We measured the resistivity up to 300 K and the absolute thermopower (TEP) up to 400 K. The temperature dependence of the resistivity follows the Mott variable-range-hopping (VRH) law $\rho = \rho_0 \exp(T_0/T)^{1/4}$ in PBCO up to ~ 100 K and in the other two systems at least up to room temperature. The results of the TEP measurements show that in YBCCO and in PBCCO the VRH probably takes place via energy states lying mainly below the chemical potential, while in PBCO this process utilizes states lying symmetrically on both sides of the chemical potential. In PBCO the TEP exhibits a cusp at low temperatures that is probably associated with the Néel point of the Pr sublattice. In PBCCO we found at low temperatures a sharp sign reversal of the TEP, from p type at high temperatures to n type at low temperatures, which needs further investigation.

I. INTRODUCTION

A common feature of most of the families of high-temperature superconductors, including the cuprate superconductors¹⁻⁵ and $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ (Ref. 6) is the existence of a nonmetallic regime in their phase diagram, characterized by hopping conductivity of charge carriers in a continuum of states. The investigation of this nonmetallic regime of the 1-2-3 family of cuprate superconductors is important both for basic research and for practical applications. The transition, as function of doping, from a metallic (superconducting) behavior to nonmetallic (nonsuperconducting) behavior may provide clues to the electronic structure of the high-temperature superconducting cuprates. On the other hand, insulating materials, that are lattice matched with the $R\text{Ba}_2\text{Cu}_3\text{O}_7$ (RBCO, where $R = \text{Y}$ or rare earth) superconductors and compatible with them in the preparation process, are required for many of the contemplated electronic devices based on superconducting films.

In the 1-2-3 family, of which $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (YBCO) is the parent member, the metal-nonmetal (MNM) transition can be induced in several ways: depletion of oxygen,² substitution of Y by Pr (Refs. 3, 7-9) or of Cu by trivalent ions such as Co (Ref. 10) and by combinations of the above. The fully oxygenated nonmetals obtained by ionic substitutions are of more interest, since they are compatible with YBCO in the preparation process.

The best known nonmetal of the 1-2-3 family is $\text{PrBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (PBCO). It is the only rare earth 1-2-3 compound which is nonsuperconducting in the orthorhombic, fully oxygenated form ($\delta \approx 0$).³ In the $\text{Pr}_x\text{R}_{1-x}\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ system (PRBCO, $R = \text{Y}$ or rare earth) with $\delta \approx 0$, the critical Pr concentration $x_c(\text{Pr})$ required for complete suppression of superconductivity in-

creases with decreasing ionic radius of R.⁹ In PYBCO one finds that $x_c \approx 0.6$, which is very close to δ_c —the critical value of the oxygen deficiency (δ) required for complete suppression of superconductivity in oxygen-depleted YBCO.

The suppression of superconductivity and the MNM transition in cobalt-doped YBCO [$\text{YBa}_2\text{Cu}_{3-x}\text{Co}_x\text{O}_{7-\delta}$ (Ref. 10) (YBCCO)] system is very similar to that in the PYBCO system. Single-phase material with $x(\text{Co})$ up to 1 can be obtained. The critical Co concentration for complete suppression of superconductivity in fully oxygenated YBCCO is $x_c(\text{Co}) \approx 0.4$. Unlike fully oxygenated PBCO which is orthorhombic, the fully oxygenated nonmetallic YBCCO is tetragonal. It has been suggested that heavily doped YBCCO may be used as a substrate for YBCO (Ref. 11) and may compete with PBCO as material for barriers and insulating layers in superlattices based on YBCO films. Below room temperature (RT) the resistivities of fully oxygenated YBCCO with $x(\text{Co}) = 1$ (Ref. 12) are higher than those of fully oxygenated PBCO. Resistivities higher by several orders of magnitude than in the last two systems have been measured in the recently synthesized, single-phase samples of fully oxygenated PBCCO with $x(\text{Co}) = 1$.¹² The early results^{8,12} showed that the temperature dependence of the resistivity of these nonmetals is typical of materials with localized carriers: it follows, up to ~ 100 K in fully oxygenated PBCO and up to room temperature, at least, in fully oxygenated YBCCO and PBCCO, the Mott variable-range-hopping (VRH) law^{13,14}

$$\rho = \rho_0 e^{(T_0/T)^p} . \quad (1)$$

This relation, with $p = \frac{1}{4}$, was derived by Mott for the case when the chemical potential resides in a band of lo-

calized states with a slowly varying, three-dimensional (3D) density of states ($p = \frac{1}{3}$ for a slowly varying, 2D density of states). $T_0 = \beta / (k_B g v)$ where g is the (constant) density of states, v is the localization volume, k_B is the Boltzmann constant and β is a numerical factor which depends on dimensionality. Different authors¹³ have obtained for β values that range from 7.6 to 39 (for 3D). According to most VRH models the dependence of ρ_0 on temperature is weak and has little effect on the analysis of the experimental results. The activation energy for hopping (in 3D) is given by $\Delta_{\text{hop}} \simeq k_B T (T_0/T)^{1/4}$ and the mean hopping distance is $R_{\text{hop}} \simeq v^{1/3} (T_0/T)^{1/4}$.

Thermoelectric power (TEP) measurements are one of the most sensitive methods for probing transport of charge carriers in materials with various conductivities. Numerous such measurements have been carried out on the new superconductors and in particular on the cuprates, where a remarkable correlation was found between the absolute thermopower S and the critical temperature for the transition to the superconducting state T_c .^{15,16} This is a promising technique also in the hopping regime despite the fact that the highly inelastic nature of the hopping process complicates the interpretation of the experimental results.

The TEP of PBCO, below RT, has been measured by Gonçalves *et al.*¹⁷ and by López-Morales *et al.*¹⁸ The main feature of the temperature dependence of S of PBCO, is a large, positive maximum, $S_m \sim 150 \mu\text{V/K}$ around 200 K. In the VRH regime, below ~ 100 K, S drops by about one order of magnitude. It should be mentioned that in the 1-2-3 family an extremum in S is frequently observed below RT. This also happens in the metallic regime (above T_c) where S has much lower values. However, the strong upward curvature in S for PBCO as temperature increases (at temperatures below that of the peak) is somewhat unusual.

We measured S in YBCCO and PBCCO where the VRH regime extends up to room temperature and also in samples of PBCO prepared under identical conditions. We tried to determine which of the features of TEP found in PBCO persist in the more resistive materials YBCCO and PBCCO and which change significantly, in the hope of being able to draw conclusions concerning the electronic structure of these materials in the vicinity of the chemical potential.

In this work we report results of a comparative study of the temperature dependence of the resistivity and absolute thermopower of *fully oxygenated* $\text{PrBa}_2\text{Cu}_3\text{O}_y$, $\text{YBa}_2\text{Cu}_2\text{CoO}_y$, and $\text{PrBa}_2\text{Cu}_2\text{CoO}_y$. The thermopower of samples of these three systems has been measured by both the Technion and the Victoria-Wellington groups.

II. EXPERIMENTAL

PBCO, YBCCO [$x(\text{Co})=1$], and PBCCO [$x(\text{Co})=1$] were prepared from high-purity Y, Pr, Cu, and Co oxides and Ba carbonate by the standard solid-state reaction. Special care was taken to ensure phase purity and good intergrain connectivity in the sintered samples. This was achieved by repeated firing (24 h at 920–950°C) and grinding cycles of the reacting material and by final pro-

longed sintering of the compacted samples (60 h at 960°C) in flowing oxygen. After slow cooling from the sintering temperature (at about 10°C/h), the samples were annealed in flowing oxygen for about a week at 350°C. They were then slowly cooled to room temperature. The resulting materials were characterized by x-ray diffraction using a Siemens D-5000 powder diffractometer with Cu $K\alpha$ radiation. Powder-diffraction spectra showed that all samples were virtually of single phase. The lattice parameters were determined by least-squares fitting of reflection peaks in the range $8^\circ \leq 2\theta \leq 120^\circ$ collected by step scan (0.02°, 4-sec step). Under the conditions of preparation described above the oxygen content in the PBCO samples is very close to 7 per formula unit ($\delta < 0.03$). Iodometric titration is problematic in the case of Co-doped samples and therefore, at present, no attempt was made to determine the oxygen content of the YBCCO and PBCCO samples. According to Ref. 10 the oxygen content may exceed 7 per formula unit in YBCCO. This may be the case also for PBCCO.

For resistance measurements, the samples had gold wires embedded prior to sintering, in a van der Pauw configuration. The resistivity was measured in a closed-cycle refrigerator, operating from room temperature down to 10 K. We tried to avoid thermal hysteresis by varying the temperature very slowly between measurements. In order to test for self-heating the I - V characteristic between the current leads was continuously checked and the current was adjusted to maintain it within the linear range. This condition becomes harder to fulfill at low temperatures as the resistance of the sample and/or of its contacts becomes very high. The most problematic seem to be the contacts of the YBCCO samples. The TEP measurements performed by both groups were as described elsewhere.^{15,19} Although the measuring system at Wellington, NZ¹⁵ can reach He temperatures, the low limit of the temperature range of the measurements was usually set by the high resistance of the samples and their contacts.

III. RESULTS AND DISCUSSION

Since it is hard to distinguish between a $T^{-1/4}$ or a $T^{-1/3}$ dependence of $\log \rho$ (VRH in 3D or in 2D), unless the temperature range extends over at least one order of magnitude, we decided to present all our results as a semilog plot of ρ versus T^{-p} with $p = \frac{1}{4}$ (see Fig. 1). Although the values of T_0 obtained from the slopes of such plots are affected by the choice of p used ($p = \frac{1}{4}$ or $p = \frac{1}{3}$), the values of the temperature-dependent activation energies [$\Delta_{\text{hop}} \propto d \ln \rho / d(1/(k_B T))$] are not affected by this choice. The results shown in Fig. 1 were obtained from samples of three batches of PBCO (1–3), YBCCO (1–3), and PBCCO (1–3). Although the preparation program, as described in the previous section, was the same for all cases, the results vary slightly from batch to batch. The temperature dependence of the resistivity of the PBCO samples agrees with that reported in the past.⁸ It follows Mott's VRH law only up to ~ 100 K. At higher temperatures the slopes of $\log \rho$ vs $T^{-1/4}$ plots are steeper, that is, the activation energies are higher. In YBCCO and

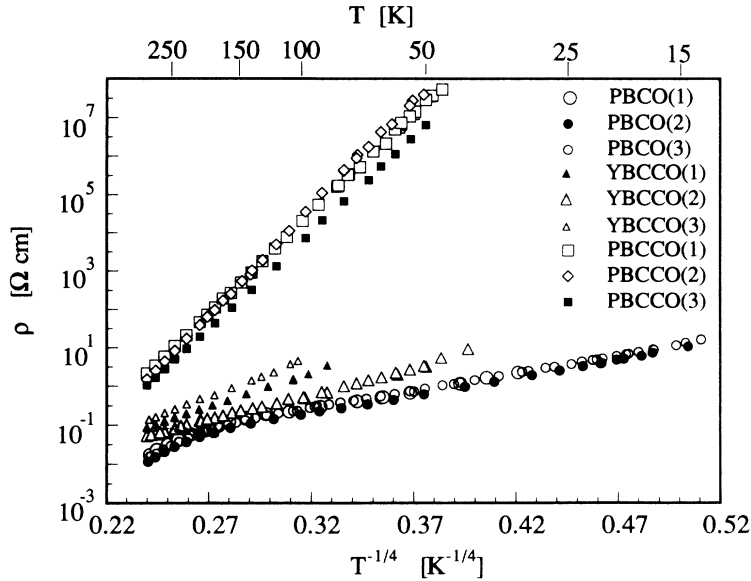


FIG. 1. Semilog plot of ρ vs $T^{-1/4}$ of PBCO, YBCCO, and PBCCO. The numbers in brackets denote the different batches. For details see text.

PBCCO the temperature dependence of ρ follows Mott's VRH law up to room temperature. The resistivities of the YBCCO samples are higher than those of the PBCO samples, by at most 1–2 orders of magnitude. However, the contact resistances to the YBCCO samples are much higher than those to PBCO and increase very fast with decreasing temperature, thus limiting the temperature range of the measurements. The results for the more resistive PBCCO samples are remarkable: for the samples with good contacts, the graphs of $\log \rho$ vs $T^{-1/4}$ are linear over *seven* orders of magnitude of ρ . Table I shows the values of T_0 and of ρ_0 , obtained from these plots and the room-temperature lattice parameters of samples of PBCO, YBCCO, and PBCCO. In view of the potential applications of these materials, we included also in the table the lattice parameters of fully oxygenated YBCO, prepared under identical conditions. While at all temperatures the resistivity of YBCCO is higher than that of PBCO, their lattice mismatch with YBCO (at room temperature) is comparable. The much higher resistivities of PBCCO are accompanied also by a greater lattice mismatch with YBCO. (Note that the *c*-axis lattice parameter of PBCCO is equal to that of YBCO).

Figure 2 shows the graphs of S vs T for several samples

of each of the three compounds. As often found, the sample with the smaller resistivity tends to have smaller thermopower. This correlation is found in samples of the same nominal composition from different batches. Also, the PBCO samples with the lowest resistivities have the lowest (positive) values of S , while those with the highest resistivities [PBCCO (2)] have the highest (positive) values of S . However, over a wide temperature range, the values of S for YBCCO (3) are higher than those of PBCCO (3) although ρ [YBCCO (3)] \ll ρ [PBCCO (3)].

The graphs for PBCO (up to room temperature) are similar to those published previously.^{17,18} In all three compounds, with decreasing temperature, S increases and passes through a maximum. In PBCO the maximum is followed by a steep drop to very low values of S . In YBCCO, the maximum is relatively shallower and in PBCCO, the maximum of S is followed by an apparent sharp reversal of sign below 100 K. Since the sign reversal occurs in a regime where the resistivity of PBCCO is very high, we suspected this feature to be either an instrumental artifact or related to contacts. However, since this sharp reversal of sign of S was observed in both our labs, it needs further investigation.

An interesting observation in the low temperature TEP

TABLE I. Crystallographic lattice constants and hopping conductivity parameters for fully oxygenated 1-2-3 compounds.

	a (Å)	b (Å)	$c/3$ (Å)	ρ_0 (Ω cm)	T_0 (K)
YBCO	3.819(1)	3.886(1)	3.893(1)		
PBCO (1)				3.8×10^{-4}	1.8×10^5
PBCO (2)				2.3×10^{-4}	2.1×10^5
PBCO (3)	3.865(1)	3.931(1)	3.905(1)	3.6×10^{-4}	1.9×10^5
YBCCO (1)				5.7×10^{-6}	3.0×10^6
YBCCO (2)	3.891(1)	3.891(1)	3.871(1)	3.4×10^{-5}	8.9×10^5
YBCCO (3)	3.892(1)	3.892(1)	3.873(1)	1.3×10^{-6}	5.4×10^6
PBCCO (1)	3.938(1)	3.938(1)	3.890(1)	6.0×10^{-13}	2.1×10^8
PBCCO (2)				5.4×10^{-14}	2.8×10^8
PBCCO (3)	3.939(1)	3.939(1)	3.893(1)	1.2×10^{-12}	1.7×10^8

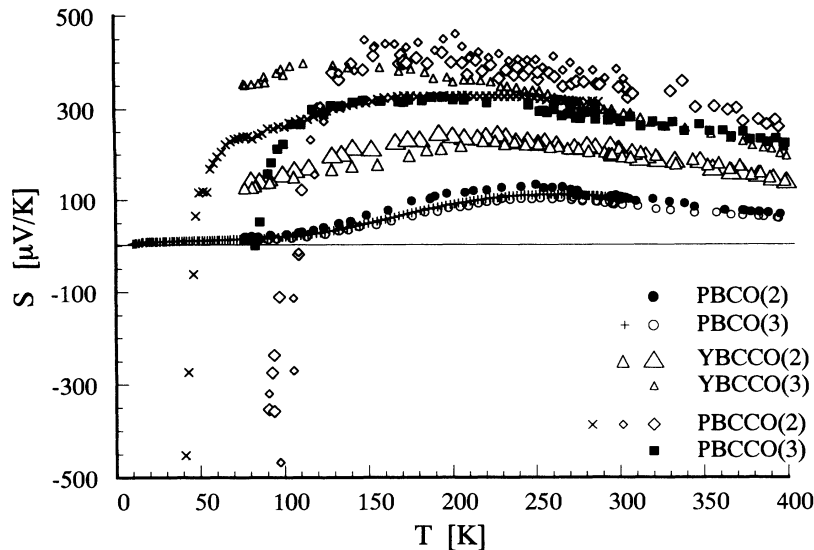


FIG. 2. S vs T for PBCO, YBCCO, and PBCCO. The numbers in brackets denote the different batches.

of PBCO is the existence (Fig. 3) of a sharp cusp at 19 K, below which the TEP is sharply reduced. We associate this cusp with the Néel temperature for the Pr sublattice. The first evidence for this transition, was the discovery of a maximum in the temperature dependence of the heat capacity of PBCO, at about 17 K, by Jee *et al.*²⁰ To check this effect, the measurements were repeated with new contacts, with essentially identical results. Another measurement on the sample after a delay of approximately four months gave similar results, with only a small shift in the low-temperature TEP, as shown in Fig. 3. This cusp resembles that illustrated by Mott and Davis¹³ at the Néel temperature in a system with hopping conduction and is also similar to the cusps observed at the Curie temperature in the TEP of ferromagnetic materials.²¹ It appears that the charge carriers at low temperatures are strongly affected by the Pr ordering.

As seen in Figs. 1–3, although the resistivities of all the samples follow Mott's VRH law rather well over wide ranges of temperatures, the temperature dependence of the thermopower is more complex, as is often the case. This is due to the high sensitivity of S to the electronic structure of the materials. We shall try now to analyze the TEP results using a more quantitative approach. The general formula for the (absolute) thermopower (S) in the hopping regime is similar to that for the diffusion TEP, derived from standard Boltzmann theory^{13,22,23}

$$S = \left(\frac{1}{|e|} \right) \left(\frac{\langle \mu - E \rangle}{T} \right). \quad (2)$$

Here, the term in brackets is the average site energy of the states participating in transport, measured from the chemical potential. The width of the energy range of the states participating in transport is $\sim \Delta_{\text{hop}} \sim k_B T (T_0/T)^{1/4}$ ($\gg k_B T$). Note that according to this relation, the component of the density of states (DOS) which is symmetric with respect to μ does not contribute to the absolute thermopower (S). Both the polarity and the magnitude of S are determined by the asym-

metry (even if it is small) of the DOS with respect to μ .²³

For the case of small asymmetry of the DOS, in 3D VRH it was shown^{13,23} that

$$S \approx \frac{k_B}{|e|} \frac{\Delta_{\text{hop}}^2}{k_B T} \left. \frac{d \ln g(E)}{dE} \right|_{E=\mu}. \quad (3)$$

Substituting for Δ_{hop} , Eq. (3) reduces to $S \propto T^{1/2}$. The same reasoning leads to $S \propto T^{1/3}$ for 2D VRH.

As seen in Figs. 2 and 3, it is difficult to fit over a reasonable temperature range a $T^{1/2}$ or a $T^{1/3}$ dependence to the experimental data of the three materials. We checked therefore whether the condition of small asymmetry, which is the basic assumption in the derivation of Eq. (3), applies here. This condition implies that the ratio

$$\begin{aligned} F &= \langle \mu - E \rangle / \Delta_{\text{hop}} \\ &= ST|e| / \Delta_{\text{hop}} \approx (S|e| / k_B)(T/T_0)^{1/4} \ll 1. \end{aligned}$$

Typical plots of F vs T are shown in Fig 4. It is seen that

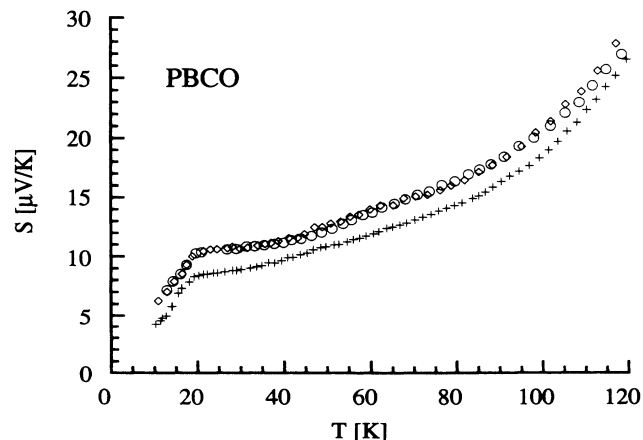


FIG. 3. Evidence for the Néel temperature of the Pr sublattice in PBCO as shown by the S versus T graphs.

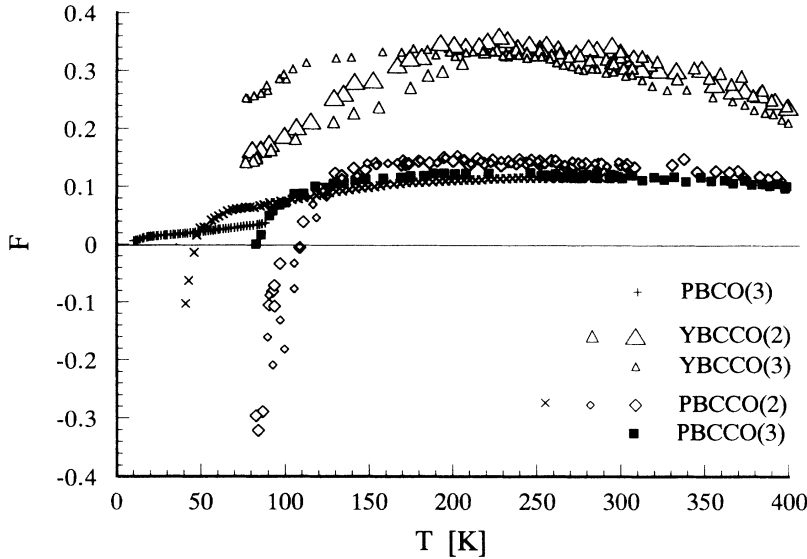


FIG. 4. F vs T calculated using data taken from Fig. 2 and the corresponding values of T_0 from Table I. For the definition of F , see text.

$F(\text{PBCO}) < 0.05$ in the range of temperatures where $\rho(\text{PBCO})$ follows Eq. (1) (up to ~ 100 K) so it might be expected that S should follow Eq. (3) in this temperature range. In fact, although S does show an increase with temperature, it is rather complex and (as mentioned above) shows a cusp at the Néel temperature. This emphasizes the greater sensitivity of S to details of the electronic structure of the material. The values of F for YBCCO and PBCCO are much higher and fall into two groups, each characteristic of one of the compounds. Interestingly, $F(\text{PBCCO})$ is almost constant (0.1–0.15) over a wide range of temperatures. This means that in that range, $\langle \mu - E \rangle$ increases with T at almost the same rate as Δ_{hop} —the energy range of states active in VRH. This is possible if the states active in hopping are located predominantly on one side of μ (in this case below μ) i.e., when μ is close to a sharp step in the density of states. The case of VRH in a band of localized states with the chemical potential lying outside this band (see Fig. 5), has been treated by Pollak,²⁴ Grant and Davis²⁵ and Zvyagin.²³ For a nondegenerate population and slowly varying DOS in a band below μ they find

$$\rho = \rho_0 \exp \left[\frac{\mu - E_0}{k_B T} + \left(\frac{T_0^*}{T} \right)^p \right], \quad (4)$$

where E_0 is the energy of the top of the band and T_0^* differs from the Mott's T_0 by a factor of the order of 2. μ is generally temperature dependent.

Zvyagin²³ showed that when the resistivity is represented by Eq. (4), the absolute thermopower (for 3D) is given by

$$S = \frac{k_B}{|e|} \left[\frac{\mu - E_0}{k_B T} + \frac{1}{4} \left(\frac{T_0^*}{T} \right)^{1/4} \right]. \quad (5)$$

According to Eq. (5), S increases with decreasing temperature, in contrast to Eq. (3) where S decreases with decreasing temperature. When the first term in brackets of Eq. (5) is small compared to the second, the first term in

brackets of Eq. (4) is also negligible and then the temperature dependence of ρ follows Mott's VRH law. In that case the value of F as defined above is $\approx \frac{1}{4}$. Figure 4 shows that above about 100 K $F(\text{YBCCO})$ varies between 0.2 and 0.35 and as mentioned above $F(\text{PBCCO})$ is about 0.1–0.15. Hence in both cases $|\langle E_0 - \mu \rangle| / k_B T < 1/4 (T_0/T)^{1/4}$; this is consistent with the temperature dependence of ρ , which follows Mott's law for the two materials. The fact that μ lies close to the upper edge of the "conduction" band of YBCCO can be accounted for by hole filling²⁶ due to the substitution of Cu^{++} by Co^{+++} , provided that the oxygen content is close to 7 per formula unit. It seems that a similar picture is obtained in PBCCO.

Now, if there is a small, but finite, density of states in the gap above E_0 , (see Fig. 5) a transition from the behavior described by Eqs. (4) and (5) to that predicted by Eqs. (1) and (3) is expected at low temperatures.²³ This

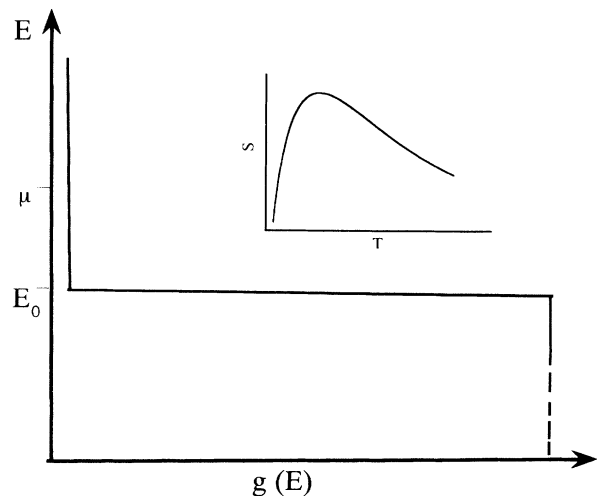


FIG. 5. Density of states as function of energy (schematic) consistent with the temperature dependence of ρ and S in YBCCO and PBCCO [after Pollak (Ref. 24)]. Inset: Temperature dependence of the TEP for the steplike DOS [after Zvyagin (Ref. 23)].

should display a maximum of S vs T , accompanied by a change in the slope of $\log \rho$ vs $T^{-1/4}$. It is possible that the shallow maximum of S vs T in YBCCO is related to this effect. Note that a break in the slope of $\log \rho$ vs $T^{-1/4}$ can be barely seen in the plot for the YBCCO(2) sample whose contacts remained finite down to 40 K.

At present, the sudden sign reversal of S of PBCCO below 100 K, with no corresponding significant changes in the temperature dependence of ρ cannot be accounted for by the above discussion and needs further experimental investigation.

Let us now return to PBCO. The low values of S and F found below 100 K are consistent with Mott's VRH theory. The change in the temperature dependence of ρ and the increase in S with increasing T may be attributed²⁷ to the onset of nearest-neighbor hopping NNH [with $p=1$ in Eq. (1)]. In a band of finite width, more than half-filled by noninteracting carriers, μ increases with temperature. In the case of fixed filling of such band, μ eventually becomes linear in temperature and S reaches its saturation value. The large maximum in S in this material seems to be of a *different* origin from that observed in YBCCO. It suggests an interplay between the tendency of S to reach a saturation value and a drop caused by excitation of carriers to a higher band. The low values of T_0 in PBCO and the low temperatures at which apparently VRH is replaced by NNH argue in favor of conduction in a narrow band with a high density of states. The higher values of T_0 in YBCCO and in particular in PBCCO and the fact that in these materials the VRH regime extends at least up to RT, shows that in these two cases conduction takes place in bands much wider than in PBCO and with much lower density of states. Note that in PBCCO the lower limit of the bandwidth is set by the RT value of $k_B T(T_0/T)^{1/4} \sim 0.75$ eV. There is no evidence in this work that in these three related systems, the bands in which conduction occurs are of the same origin, e.g., all are related to the CuO_2 planes. We plan to continue to investigate this problem by carrying out a systematic study of the YBCCO and PBCCO systems as a function of $x(\text{Co})$.

IV. CONCLUSIONS

The main experimental results of this work and their implications can be summarized as follows:

(1) The temperature dependence of the resistivity follows the Mott (VRH) law in PBCO up ~ 100 K and in YBCCO and PBCCO up to at least room temperature.

(2) We obtained $T_0(\text{PBCO}) < T_0(\text{YBCCO}) \ll T_0(\text{PBCCO})$, hence we conclude that the corresponding products of the DOS and the localization volume follow $gv(\text{PBCO}) > gv(\text{YBCCO}) \gg gv(\text{PBCCO})$.

(3) TEP measurements show that the VRH in PBCO probably takes place through electron energy states below and above μ . At high temperatures VRH is probably replaced by NNH in a *partially* filled band.

(4) A cusp exhibited by the TEP of PBCO at low temperatures is associated with the Néel temperature of the Pr sublattice.

(5) TEP measurements indicate that in YBCCO and in PBCCO the VRH takes place via electron states located mainly below μ , i.e., the DOS is asymmetric with respect to μ . Hence, in these materials, μ presumably lies near the edge of an almost full band.

(6) In PBCCO the sign reversal of S at low temperatures, apparently without corresponding changes in the temperature dependence of ρ , is not understood and needs further investigation.

(7) At present there is no evidence whether in all the three related systems the bands of states taking part in conduction are derived from the same origin, e.g., the CuO_2 planes.

Noted added in proof. In the meantime, the oxygen content of fully oxygenated YBCCO and PBCCO samples has been determined by iodometric titration. The results are: 7.33 in YBCCO and 7.29 in PBCCO. We are grateful to Dr. A. Knizhnik for these measurements.

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