Low-temperature charge transport in $PrBa_2Cu_4O_8$: Electronic states of the doped Cu-O chain

I. Terasaki, N. Seiji, S. Adachi, and H. Yamauchi*
Superconductivity Research Laboratory, International Superconductivity Technology Center, 1-10-13 Shinonome, Koto-ku, Tokyo 135, Japan
(Received 3 June 1996; revised manuscript received 15 July 1996)

Transport parameters in $PrBa_2Cu_4O_8$ have been measured and analyzed. The charge transport arising from the Cu-O double chain is consistently explained in terms of the one- to two-dimensional (1D-2D) crossover around 100 K, where the system becomes 1D (2D) at high (low) temperatures. This is characterized by the rapid increase in the Hall coefficient and the magnetoresistance below 100 K, and also by the small thermopower below 100 K. [S0163-1829(96)07542-X]

Electron correlation in low-dimensional systems has been one of central subjects in recent solid-state physics since the discovery of high-temperature superconductors (HTSC's). Above all, a metallic one-dimensional (1D) Cu-O chain is of particular interest. First, such a system can be a model material for the 1D Hubbard Hamiltonian that has been recently solved exactly.[1] Second, in a 1D conductor, the spin and charge degrees of freedom are separated to form the Luttinger liquid, a ''well-defined'' non-Fermi liquid.[2] Third, undoped Cu-O chains show a quantum spin nature, e.g., a spin-Peierls transition in $CuGeO_3$,[3] and unusually low Néel temperature in Sr_2CuO_3.[4] In spite of these prospects, no one has succeeded so far in preparing a metallic Cu-O chain by doping.[5]

A possible candidate for a metallic Cu-O chain is $PrBa_2Cu_4O_8$ (Pr-124).[6,7] As is similar to $PrBa_2Cu_3O_7$ (Pr-123),[8] Pr-124 is a nonsuperconductor with the CuO_2 plane. Although various models have been proposed to explain the origin of the suppression of superconductivity in Pr-123, it is still an open question.[9] At least we can say that Pr-123 has too few carriers (or too small Drude weight) in the CuO_2 plane to cause superconductivity, which is suggested from transport[10] and optical[11] measurements. A significant difference between Pr-123 and Pr-124 is that the latter is a good metal at low temperatures.[6,7] As listed below, many facts strongly suggest that the Cu-O double chain in Pr-124 is responsible for the metallic nature. (i) As shown in the inset of Fig. 1, the only difference in the crystal structure between Pr-123 and Pr-124 is in the Cu-O chain structure (the hatched area in the inset). It is thus natural to attribute the different physical properties to the different part in the crystal structures. (ii) The Cu-O chain in Pr-123 is essentially metallic. Takenaka *et al.*[11] have reported that the *b*-axis optical conductivity in Pr-123 (along the chain) has a large Drude weight. Hoffmann *et al.*[12] have observed a Fermi surface related to the Cu-O chain in Pr-123 through positron-annihilation measurement. Lee, Suzuki, and Geballe[13] have shown that Pr-123 films with less disorder exhibit more metallic charge transport attributable to the Cu-O chain. Accordingly we can expect the Cu-O double chain in Pr-124 to be more metallic than the Cu-O chain in Pr-123, because the oxygen vacancies as well as the effects of disorder are less in the former. (iii) A site-selective substitution study has indicated that the Cu-O double chain is responsible to the metallic conduction in Pr-124. Yamada *et al.*[14] reported that doped Zn cations (mainly substituted for Cu in the CuO_2 plane) essentially unaltered the metallic conduction, while doped Ni cations (partly substituted for Cu in the CuO double chain) made the sample semiconductive.

Here we present an observation on the Hall coefficient, thermopower, and magnetoresistance of $PrBa_2Cu_4O_8$. All the parameters are strongly dependent on temperature (T), whose T dependence is quite different from that of HTSC's or conventional metals. The unusual T dependence is well explained from the viewpoint of the crossover from one to two dimensions (1D-2D) where the interchain hopping energy of the order of 100 K overcomes thermal fluctuation k_BT at low temperatures. This is evidenced by the rapid increase in the Hall coefficient and the magnetoresistance and the extremely small thermopower below 100 K.

Polycrystalline samples of $PrBa_2Cu_4O_8$ were prepared by a solid-state reaction technique as was reported previously.[6] The x-ray-diffraction pattern of the samples showed no trace of Pr-123 phase within the experimental resolution. Although it detected a tiny trace ($<3\%$) of $BaPrO_3$ and/or $BaCuO_2$, we expect that they will not affect the transport properties seriously because of their highly insulating nature. We should note that the impurity phases are much less in the present samples than in the previous study

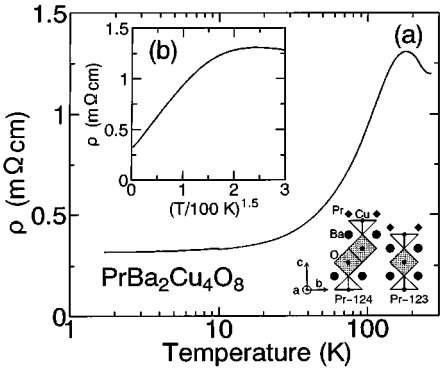

FIG. 1. (a) Temperature dependence of the resistivity ρ of $PrBa_2Cu_4O_8$. The crystal structures of $PrBa_2Cu_4O_8$ (Pr-124) and $PrBa_2Cu_3O_7$ (Pr-123) are schematically drawn in the inset. (b) ρ plotted as a function of $(T/100\ \mathrm{K})^{1.5}$.

of Ref. 6. The lattice constants were equal to the values extrapolated from the data of $Y_{1-x}Pr_xBa_2Cu_4O_8$ in the limit of $x \rightarrow 1$, which further evidenced that the prepared samples are truly Pr-124.

Resistivity (ρ) and magnetoresistance ($\Delta\rho/\rho$) were measured using a conventional four-probe method in magnetic fields (H) of 0–8 T perpendicular to the current. Hall coefficient (R_H) was measured in a six-probe configuration, where H was swept from -6 to 6 T to eliminate the zero-field signal and the magnetoresistance due to the misalignment of the voltage contacts. For thermopower (S), one edge of the sample was pasted on a sapphire plate acting as a heat bath, while the other edge was pasted on another sapphire plate with a sheet heater. The temperatures on the edges were monitored through two diode thermometers pasted near each edge.

Figure 1(a) shows the temperature dependence of the measured resistivity of $PrBa_2Cu_4O_8$. The resistivity takes a maximum near 170 K, below which it exhibits a metallic conduction, as is reported in the literature.[6,7] As shown in Fig. 1(b) in which ρ is plotted as a function of $(T/100\ \mathrm{K})^{1.5}$, ρ is roughly expressed by $\rho=\alpha T^{1.5}+\rho_0$ below 100 K.[15] Yamada *et al.*[7] reported a slight upturn in ρ below 4.2 K, but we did not observe any increase in ρ from 170 down to 1.4 K. Thus the upturn is possibly extrinsic, and can be ascribed to localization effects.

First of all, we examine here whether we can neglect the contribution of the carriers in the CuO_2 plane or not. For this purpose, we measured Cu NMR of Pr-124 and found that the spins of the CuO_2 plane exhibit a Néel order below 250 K.[16] We should also note that a recent muon-spin-relaxation measurement has also revealed the Néel order below 200 K.[17] Since the resistivity of antiferromagnetically ordered CuO_2 planes is very high at low temperatures (typically more than 0.1 Ωcm below 100 K), it would be more than three orders of magnitude higher than the observed resistivity of Pr-124 below 100 K. Regarding the conduction in Pr-124 as a parallel circuit consisting from plane and chain, we expect that less than 1% of the current would flow in the CuO_2 plane at low temperatures. Thus we safely neglect the contributions of the CuO_2 plane to the charge transport below the Néel order. On the other hand, we have to consider the CuO_2 plane above the Néel order, which might be responsible for the broad maximum of the resistivity near 170 K.

Positive R_H indicates that mobile carriers are holes, as shown in Fig. 2. While the magnitude of R_H at room temperature (2×10^{-4} cm^3/C) is small, comparable to the resolution of our measurement (1×10^{-4} cm^3/C), it rapidly increases below 100 K to saturate around 1.2×10^{-3} cm^3/C below 10 K. Similar T dependence of R_H has been reported in Pr-123 (Ref. 13) and $La_5SrCu_6O_y$.[18] It should be emphasized that a purely 1D metal gives no Hall voltage because the Lorentz force cannot bend a trajectory of a mobile carrier across the conducting chain. Even if there exists a finite interchain hopping energy ($t_\perp$), the Hall conductivity remains quite small for an open Fermi surface.[19] At low temperatures where $t_\perp$ is much larger than k_BT, the system begins to show a quasi-2D nature, and consequently the Lorentz force becomes effective to increase R_H. Thus we regard the temperature dependence of R_H as a sign of the 1D-2D crossover. The crossover will occur around $t_\perp \sim k_BT$, and accordingly the interchain hopping energy is estimated to be of the order of 100 K.[20]

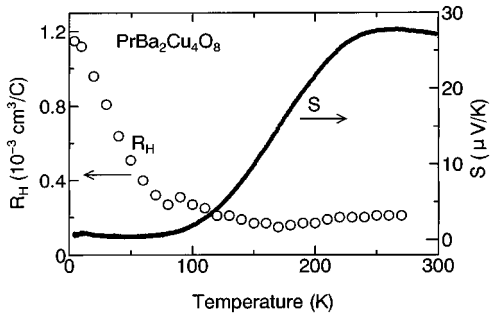

FIG. 2. Temperature dependence of the Hall coefficient R_H (open circles) and the thermopower S (solid curve) of $PrBa_2Cu_4O_8$.

Positive S also indicates that the doped carriers are holes, as shown in Fig. 2. Contrary to R_H, S is large at room temperature (27 μV/K), and rapidly decreases below 250 K. The magnitude of S below 100 K is quite small (less than 1 μV/K), which is ascribed to the quasi-2D nature in the low-temperature electronic states in Pr-124. Under the lowest-order approximation, S is proportional to the energy derivative of the density of states (DOS), and hence nearly free carriers in a 2D metal, whose DOS is energy independent, will give no thermopower.

The magnetoresistance (MR) shown in Figs. 3(a) and 3(b) is further evidence for the 1D-2D crossover. We have assigned MR in Pr-124 to classical MR—the change in the trajectories of carrier motions induced by the Lorentz force—by the following reasons. The longitudinal MR, showing *identical* T dependence to the transverse MR, is smaller in magnitude.[21] In addition, all the measured MR is positive, and roughly proportional to H^2. The third reason is that a similar MR in Pr-123 has been assigned to classical MR.[13] Our assignment is consistent with the assumption that the metallic nature is responsible for the Cu-O double chain, because the carriers in the CuO_2 plane would be scattered by the adjacent Pr $4f$ spins to cause isotropic and negative MR. We further note that we did not observe any trace of negative MR at all temperatures, which means that neither spin scattering nor localization is significant in the magnetoresistance in Pr-124.

Classical MR in metals is roughly equal to $(\omega_c\tau)^2$ (ω_c and τ are the cyclotron frequency and the scattering time, respectively). In other words, $\Delta\rho/\rho$ in conventional metals follows a scaling function of $(H/\rho)^2$, which is known as Kohler's rule.[22] Figure 3(a) shows the measured MR with $I \perp H$ as a function of $(H/\rho)^2$, clearly indicating the violation of Kohler's rule. We can understand this violation by introducing the T dependent ω_c on the basis of the 1D-2D crossover. At high temperatures ($k_BT \gg t_\perp$), the system will act as a 1D conductor to give $\omega_c \sim 0$, whereas the system will be 2D to have a finite ω_c for $k_BT \ll t_\perp$. To evaluate the T-dependent ω_c, we rewrite the relation of $\Delta\rho/\rho \sim (\omega_c\tau)^2$ as $\Delta\rho/\rho \sim (AH/\rho)^2$, where A is a T-dependent constant. In Fig. 3(b), we plotted A calculated from $\sqrt{\rho\Delta\rho}/H$ at 8 T as a

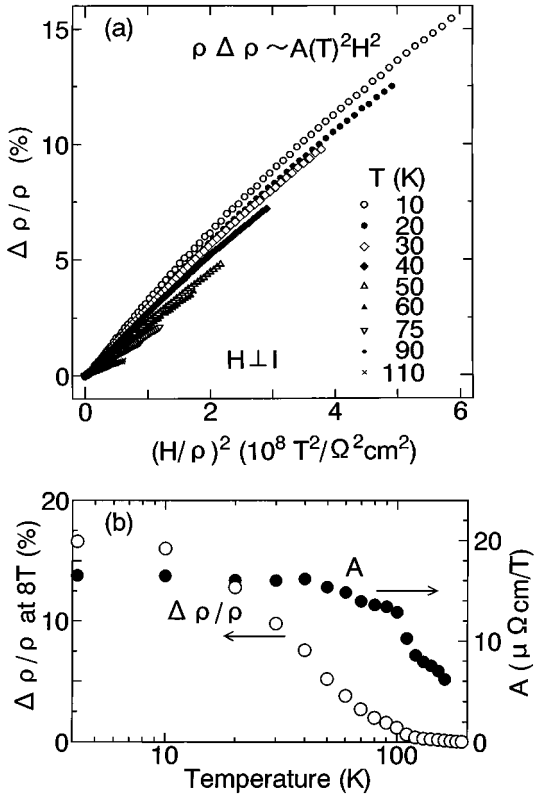

FIG. 3. (a) Transverse magnetoresistance $\Delta\rho/\rho$ plotted as a function of $(H/\rho)^2$, where H is the applied field and ρ is the zero-field resistivity. (b) $\Delta\rho/\rho$ at 8 T and $A(T)\equiv\sqrt{\rho(T,0)\Delta\rho(T,H)}/H$ plotted as a function of temperature.

function of temperature. As is expected, $A(T)$ is nearly constant at low temperatures, and rapidly decreases with T above 100 K.

Here let us discuss the anisotropy between the inter- and intrachain hopping energies. As discussed above, we have found $t_\perp$ to be around 100 K, and we expect that the intrachain hopping energy $t_\parallel$ is the same as the in-plane hopping energy in HTSC's, ~1000 K. As a result, $t_\parallel/t_\perp$ is estimated to be about 10, comparable to the anisotropy in $(TMTSF)_2ClO_4$, a quasi-1D organic conductor.[23] One may doubt whether the estimated $t_\parallel/t_\perp$ is smaller than is expected from the crystal structure, but we think that the estimation is reasonable by comparison with the band calculation for $YBa_2Cu_4O_8$.[24] The recent measurement using untwinned Pr-123 crystals by Eisaki *et al.* has shown that the interchain resistivity in Pr-123 is about one order of magnitude larger than the intrachain one,[25] which is well consistent with our estimation.

Finally we would like to add some comments on the electronic states in Pr-124. (a) As mentioned above, we cannot estimate the carrier concentration from $1/R_H$ because of the highly 1D electronic states of Pr-124. It is generally agreed that the only way to estimate the carrier concentration in a 1D conductor is to analyze S. The observed S above 250 K very weakly depends on temperature, where the transport part in S seems negligibly small. If so, we can employ the Heikes formula expressed as $S=(k_B/e)\ln[2(1-x)/x]$ (x is the hole concentration per Cu in a chain),[26] and obtain $x\sim0.5$, which is comparable to the Drude weight of the Cu-O chain in Pr-123.[11] (b) Matsushita *et al.*[27] have reported that pressure enhances the low-T metallic conduction in Pr-124. This can be also explained within the framework of the 1D-2D crossover. We can assume, at least qualitatively, that the applied pressure shrinks the lattice to increase $t_\perp$. Since the crossover is determined by $k_BT\sim t_\perp$, the pressure would raise the crossover temperature and stabilize the low-temperature electronic states in Pr-124. (c) Through the present study, we can estimate the Cu-O chain contribution to the conductivity in $YBa_2Cu_3O_7$ and $YBa_2Cu_4O_8$. Owing to the 1D nature above 100 K, the interchain contribution is negligible in the normal state, which naturally suggests that the a- and c-axis resistivity is dominated by carriers in the CuO_2 plane. We can also regard the b-axis conductivity as a simple summation of the plane and chain conductivities. On the other hand, the in-plane Hall coefficient is seriously affected by the presence of conducting Cu-O chains. Since the Cu-O chain is 1D above 100 K, it gives very small Hall voltage. In a real experiment, Hall bars electronically short the CuO_2 plane to the Cu-O chain, and decrease the Hall voltage in the plane as low as that in the chain. This is evidenced by the anomalously small Hall coefficient of $YBa_2Cu_4O_8$.[28]

In summary, we have presented a measurement on the Hall coefficient, thermopower, and magnetoresistance of $PrBa_2Cu_4O_8$. We have shown that their temperature dependence can be consistently explained in terms of the 1D-2D crossover around 100 K. Below 100 K, reflecting the quasi-two-dimensional nature, $PrBa_2Cu_4O_8$ shows large Hall coefficient and magnetoresistance and a quite small thermopower. Above 100 K, the Hall coefficient and the magnetoresistance rapidly decrease with temperature, implying that the Lorentz force does not work owing to the one-dimensional nature. Thus the interchain hopping energy is estimated to be about 100 K, which is one order of magnitude smaller than the intrachain hopping energy.

We would like to thank S. Uchida, H. Eisaki, Y. Yamada, N. Yamada, M. Ogata, H. Takagi, Y. Enomoto, and K. Tanabe for fruitful discussions. This work was partially supported by NEDO for R&D of Industrial Science and Technology Frontier Program.

*Present Address: Research Laboratory of Engineering Materials, Tokyo Institute of Technology, 4259 Nagatsuda, Midori-ku, Yokohama 227, Japan.

[1] N. Kawakami and S.-K. Yang, Phys. Lett. **148A**, 359 (1990); Phys. Rev. Lett. **65**, 2309 (1990); N. Kawakami and A. Okiji, Prog. Theor. Phys. Suppl. **108**, 251 (1992).

[2] M. Ogata and H. Shiba, Phys. Rev. B **41**, 2326 (1990); N. Kawakami, Batsuri **46**, 565 (1991) (in Japanese).

[3] M. Hase, I. Terasaki, and K. Uchinokura, Phys. Rev. Lett. **70**, 3651 (1993).

[4] A. Kerren *et al.*, Phys. Rev. B **48**, 12 926 (1993); T. Ami *et al.*, *ibid.* **51**, 5994 (1995).

[5] For $CuGeO_3$, the transfer energy between Cu $3d$ and O $2p$ is too small for metallization. See, I. Terasaki *et al.*, Phys. Rev. B **52**, 295 (1995).

[6] N. Seiji, S. Adachi, and H. Yamauchi, Physica C **227**, 377 (1994).

[7] Y. Yamada *et al.*, Physica C **231**, 131 (1994).
[8] For a recent review on $PrBa_2Cu_3O_7$, H. B. Radousky, J. Mater. Res. **7**, 1917 (1992).
[9] R. Fehrenbacher and T. M. Rice, Phys. Rev. Lett. **70**, 3471 (1993); A. I. Liechtenstein and I. I. Mazin, *ibid.* **74**, 1000 (1995).
[10] Pr substitution in $Y_{1-x}Pr_xBa_2Cu_3O_7$ increases the Hall coefficients. See, for example, W. Jiang *et al.*, Phys. Rev. B **46**, 8694 (1992); Y. X. Jia *et al., ibid.* **46**, 11 745 (1992).
[11] K. Takenaka *et al.*, Phys. Rev. B **46**, 5833 (1992).
[12] L. Hoffmann *et al.*, Phys. Rev. Lett. **71**, 4047 (1993).
[13] M. Lee, Y. Suzuki, and T. H. Geballe, Phys. Rev. B **51**, 15 619 (1995).
[14] Y. Yamada *et al.* (unpublished).
[15] In contrast to Pr-124, the Cu-O double chain in $YBa_2Cu_4O_8$ shows T^2-linear resistivity. [See for example, B. Bucher and P. Wachter, Phys. Rev. B **51**, 3309 (1995).]
[16] J. Kikuchi *et al.* (unpublished).
[17] T. Tatsumi *et al.* (unpublished).
[18] Y. Enomoto *et al.*, Phys. Rev. B **42**, 6773 (1990).
[19] N. P. Ong, Phys. Rev. B **43**, 193 (1991).
[20] This discussion is valid only in the high-field limit or in a single-carrier model. We expect that the latter case is realized in Pr-124, that is, the carriers in Pr-124 are mainly holes. Since the maximum field of 8 T in the present study is still lower than for the high-field limit ($\omega_c\tau \sim 4\%$), R_H can be, in general, T dependent in the presence of holes and electrons. However, the combination of R_H with $\Delta\rho/\rho$ allows us to neglect the contribution of electrons. In a two-carrier model, the very small R_H above 100 K means that the concentrations of the two are nearly equal, which would give a large $\Delta\rho/\rho$. The experimental data are just opposite, where R_H is roughly proportional to $\sqrt{\Delta\rho/\rho}$.
[21] Since we used polycrystals, some of the randomly distributed current paths will locally violate the condition of $H||I$ to make the Lorentz force effective. As a result, classical MR can be observed in the longitudinal configuration in polycrystals.
[22] A. B. Pippard, *Magnetoresistance in Metals* (Cambridge University Press, Cambridge, 1989).
[23] For a review, see T. Ishiguro and K. Yamaji, *Organic Superconductors* (Springer-Verlag, Berlin, 1990).
[24] S. Massidda *et al.*, Physica C **176**, 159 (1991); J. Yu, K. T. Park, and A. J. Freeman, *ibid.* **172**, 467 (1991).
[25] H. Eisaki *et al.* (unpublished).
[26] For the Heikes formula with the strong correlation, see, for example, MD. A. Malik, *et al.*, Mod. Phys. Lett. B **8**, 947 (1994), and references therein.
[27] A. Matsushita *et al.*, Physica C **242**, 381 (1995).
[28] B. Bucher *et al.*, Phys. Rev. Lett. **70**, 2012 (1993).