Transport Properties of a $YBa_2Cu_4O_8$ Crystal under High Pressure

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(Received 1 May 1996)

Measurements of the temperature dependence of the resistivity ρ_a, ρ_b, resistance R_c, and thermoelectric power $\alpha_a, \alpha_b, \alpha_c$ for a $YBa_2Cu_4O_8$ crystal under high pressure verify that the CuO_2 sheets are oxidized by pressure-induced electron transfer from the CuO_2 sheets to the Cu(1)-O double chains. The anomaly in the CuO_2-sheet resistivity ρ_a at $T \approx 170$ K, which moves to a higher temperature on oxidation of the CuO_2 sheets, is correlated to a change in the character of R_c. Our data also demonstrate unambiguously the contribution to the transport properties from Cu-O chains. [S0031-9007(96)01634-1]

PACS numbers: 74.25.Fy, 72.15.Jf

In this Letter we report measurements on single-crystal $YBa_2Cu_4O_8$ of resistivity and thermoelectric power (TEP) versus temperature T along **a**, **b**, and **c** axes individually and their behavior under high pressure. Naturally stoichiometric (no dopants or oxygen vacancies) $YBa_2Cu_4O_8$ is chemically stable (no observable weight or structural change to 850 °C [1]) and twin free [2]; yet it contains underdoped CuO_2-Y-CuO_2 superconductive layers separated by BaO-Cu_2O_2-BaO_2 layers having edge-shared Cu(1)-O charge-reservior double chains perfectly oriented parallel to the orthorhombic **b** axis. A single-crystal measurement of $\rho_a(T)$ and TEP $\alpha_a(T)$ avoids any chain contribution to the conductivity of the CuO_2 sheets. We have therefore been able to verify the widely held assumption, for example [2–4], that pressure induces electron transfer from the CuO_2 sheets to the Cu(1)-O double chains, and we use pressure to vary the Cu(III)/Cu ratio in the CuO_2 sheets without chemical doping. This procedure allows us to show the following: (a) the previously observed [5] anomaly in $\rho_a(T)$ at a temperature T_D is inconsistent with an opening of a spin gap below T_s, but may be associated with a change in the **c**-axis resistance $R_c(T)$; (b) a correlation of T_c with a low-temperature enhancement $\delta\alpha(T)$ of the TEP supports our earlier claim that this correlation is a general property of the copper oxides; (c) an important negative contribution to the **b**-axis TEP $\alpha_b(T)$ from metallic and superconductive Cu(1)-O double chains; and (d) a correlation between the superconductive-pair concentration n_s within the chains and the chain contribution to the enhancement $\delta\alpha(T)$ in the TEP.

Single crystals were grown under high oxygen pressure [6] with a maximum size of $1.2 \times 0.4 \times 0.1$ mm. ac susceptibility, e.g., Fig. 1, showed that superconductivity at $T_c \approx 81$ K in all crystals used is not filamentary. The resistive transition at T_c, e.g., Fig. 3, is extremely sharp. The Montgomery method, which is suitable for platelike samples with a strongly anisotropic conductivity, was used to measure ρ_a and ρ_b; R_c was obtained with a simple four-probe method. In all cases, Cu wires 10 μm in diameter were attached to the crystal with silver epoxy. All high-pressure measurements were carried out in a self-clamped apparatus with silicone oil as a pressure medium and manganin coil as a manometer. We have monitored the pressure at all temperatures for each experiment. The cooling rate is controlled at 0.2 K/min in order to maintain hydrostatic pressure. The Cu-lead contribution was subtracted from all TEP measurements. Because of some uncertainty in the measurements of the geometric factor the calculated magnitude of the resistivity has an uncertainty of 20% about the value given, and we have plotted the resistance $R_c(T)$ rather than $\rho_c(T)$. We define T_0 as the temperature below which the resistance vanishes with a nanovolt meter; we use the pressure P at T_0 in our calculation of dT_0/dP. All the measurements have been carried out on the same crystal, and the basic features of the results were reproduced in another crystal. The ambient-pressure value of $\rho(T)$ and $\alpha(T)$ was recovered after releasing the pressure.

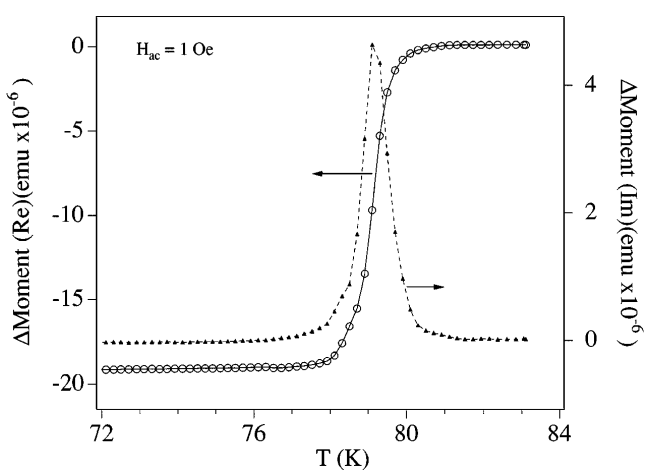

FIG. 1. ac susceptibility versus temperature for a $YBa_2Cu_4O_8$ crystal.

Figures 2(a) and 3(a) show, respectively, ρ_a and ρ_b versus temperature for several pressures. The ambient-pressure data are consistent with the literature [5], i.e., a change in slope of ρ_a vs T near 170 K, a Bloch-Grüneisen (BG) conductivity along the **b** axis, and a $\rho_a(300\text{ K})/\rho_b(300\text{ K}) \approx 4$ that is indicative of a higher conductivity along the double chains than in the CuO_2 sheets. Pressure reduces ρ_a dramatically with a coefficient $d(\ln\rho_a)/dP \approx -0.014\ (\text{kbar})^{-1}$, whereas a $d(\ln\rho_b)/dP \approx -7.8 \times 10^{-4}\,(\text{kbar})^{-1}$ shows a weak pressure dependence of the chain's resistivity. After taking into account the difference in the compressibility, which is a factor of 2 [4], the resistivity changes with respect to the lattice-parameter change along the **a** and **b** axes show a large difference $(d\ln\rho_a/d\ln a)/(d\ln\rho_b/d\ln b) \approx 10$. The superconductive transition increases with hydrostatic pressure. A $dT_0/dP \approx 0.58 \pm 0.02$ K/kbar was obtained from measurements of the resistivity and TEP along **a**, **b**, and **c** axes. This dependence is similar to that obtained with polycrystalline and single-crystal samples [4,7]; it has been widely assumed to indicate a pressure-induced electron transfer from the CuO_2 sheets to the double chains. Although this inference is supported by high-pressure neutron-diffraction refinement [2,3], measurement of the pressure dependence of the TEP, $d\alpha/dP$, can provide the surest verification of this conjecture.

Figures 2(b) and 3(b) show, respectively, the TEP α_a and α_b versus temperature for several pressures. At ambient pressure and temperature, the slope of α_a vs T is negative, whereas that of α_b vs T is positive. The α_a curve reflects the contribution from the CuO_2 sheets; it is similar to the α_a obtained on a fully oxidized, perfectly detwinned $YBa_2Cu_3O_{7-\delta}$ crystal [8] and also on polycrystalline cuprates having no charge reservoir in the intergrowth layer [9,10]. The sharp difference between α_a and α_b unambiguously demonstrates strong anisotropy due to the existence of one-dimensional Cu-O chains. The positive slope of α_b vs T that is introduced by the dominant chain contribution thus confirms our earlier deduction from polycrystalline measurements of a negative TEP enhancement from the chains below 300 K in both $YBa_2Cu_3O_{7-\delta}$ and $YBa_2Cu_4O_8$ samples [4,11].

R_c shows a semiconductor behavior below room temperature followed, on cooling, by a change of curvature near $T \approx 170$ K, Fig. 4(a). The TEP along the **c** axis, Fig. 4(b), is small and only weakly dependent on temperature and pressure, which indicates that neither a band model nor a simple polaronic model is appropriate to describe the **c**-axis transport.

The highly anisotropic resistivity, $\rho_a(300\text{ K})/\rho_b(300\text{ K}) \approx 4$, indicates that the crystal is of high quality because any contamination from the crucible, for example Al, reduces the conductivity from the Cu-O chains. Under high pressure, ρ_a and ρ_b behave differently; a derived ratio $(d\ln\rho_a/d\ln a)/(d\ln\rho_b/d\ln b)$ is about 10. To interpret this ratio, a pressure-induced charge transfer between CuO_2 sheets and Cu-O chains, which is verified by the TEP results, as well as band broadening under pressure, should be taken into account. In a classical picture of metallic conduction, only a small

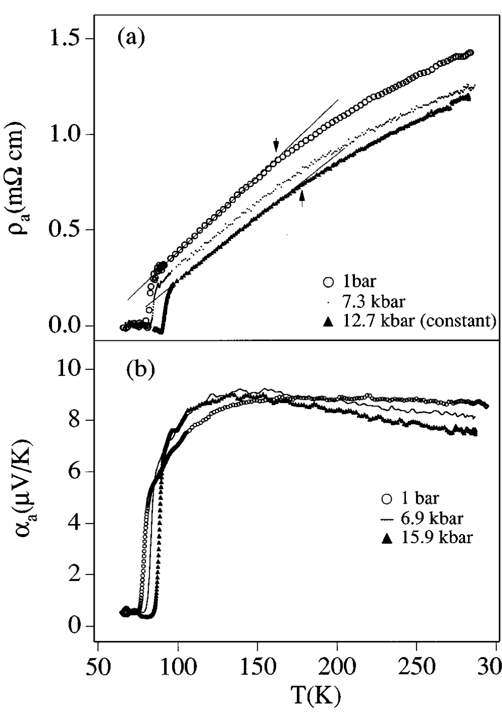

FIG. 2. The resistivity (a) and TEP (b) along the **a** axis versus temperature under several pressures. The curve of 12.7 kbar has been corrected to a constant pressure.

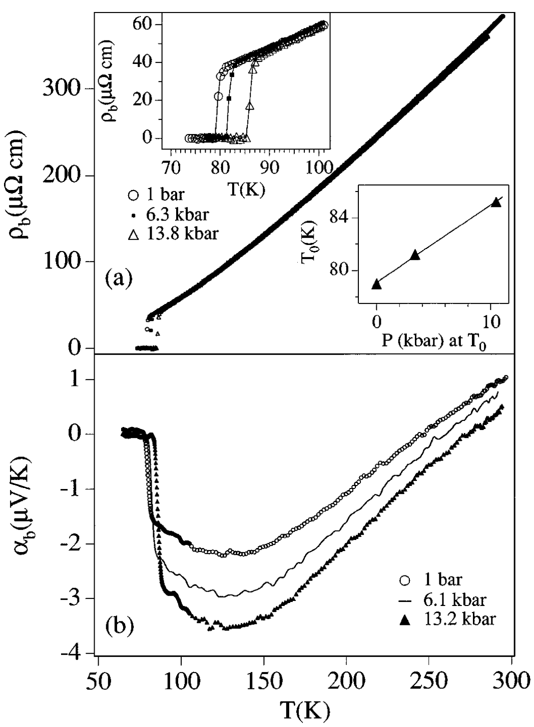

FIG. 3. The resistivity (a) and TEP (b) along the **b** axis versus temperature under several pressures. Inset: detail of the resistivity near transition temperature and superconductive transition temperature T_0 versus pressure.

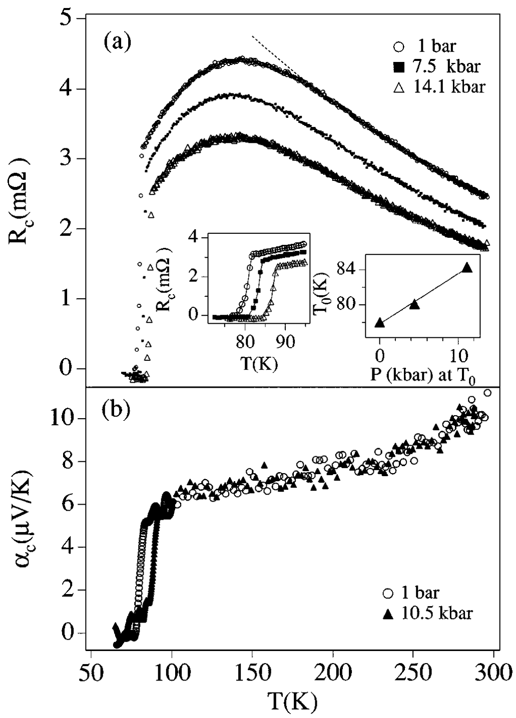

FIG. 4. The resistance (a) and TEP (b) along the **c** axis versus temperature under several pressures. The dashed line is an exponential fitting to the resistance at 1 bar. Inset: detail of the resistivity near transition temperature and superconductive transition temperature T_0 versus pressure.

fraction of electronic states near E_F, i.e., kT/E_F, are involved in the transport. Band broadening by pressure or shifting of the Fermi level should not influence the conductivity remarkably. The temperature and pressure dependence of ρ_b are typical of conventional conduction. The conduction in the CuO_2 sheets, however, is very sensitive to the charge carrier density. The temperature dependence of ρ_a is also different from that of a conventional metal, say a BG conduction, and that of other cuprate superconductors. There are two temperature ranges where ρ_a shows a linear dependence (Bucher *et al.* [5] have demonstrated the linear dependence in the high-temperature range). A change of slope occurs over a broad temperature range near 170 K. Under high pressure, this same feature is maintained. The low temperature part of ρ_a above T_c has been fit to a linear curve. The temperature where ρ_a deviates from this linear dependence, as marked with an arrow in Fig. 2(a), moves to a higher value under pressure. Bucher *et al.* [5] have referred to the temperature of this change of slope in ρ_a as T_D, and they suggested it correlates with the opening of a spin gap at T_s in the underdoped cuprates. Opening a spin gap would eliminate a spin-scattering channel so as to enhance the conductivity below T_s. If this is the case, the linear temperature dependence of ρ_a in the range $100 \leq T \leq 150$ K would represent a state in which the scattering is caused by nonmagnetic interactions.

A spin gap has been predicted by magnetic models [12] and confirmed by NMR [13,14] in the underdoped cuprates. According to these models and experimental data, T_s falls below T_c at optimal doping. If T_D is to be associated with T_s, the linear part of ρ_a vs T at low temperature should disappear at optimal doping. High pressure induces a charge transfer, which is verified by a decrease of α_a under pressure, see Fig. 2(b), and also by a large coefficient $dT_c/dP \approx 0.59$ K/kbar. This pressure-induced charge transfer adds holes to the CuO_2 sheets and electrons in the Cu-O chains. Since T_c moves to 86 K from 81 K under the pressure used, T_s should drop significantly. Therefore the temperature range in which ρ_a vs T shows a linear dependence above T_c should be reduced under high pressure, a prediction that is inconsistent with what we observed. Moreover, the low-temperature extrapolation of this linear part in ρ_a vs T intersects a negative resistivity at $T = 0$ K. The same feature has been found in ρ_a of a twin-free, fully oxidized Y-123 crystal in which the CuO_2 sheets are slightly overdoped [15].

In the superconductive copper oxides, the CuO_2 sheets have a TEP $\alpha = \alpha_0 + \delta\alpha(T)$, where α_0 is determined by the hole concentration; the enhancement term $\delta\alpha(T)$ has a characteristic maximum at a $T_{\max} \approx 140$ K and decays to near zero by 300 K, where an $\alpha(300\text{ K}) \approx \alpha_0$ is found [9]. Therefore the reduction of $\alpha_a(300\text{ K})$ by pressure, Fig. 2(b), verifies the inference that pressure oxidizes the CuO_2 sheets by electron transfer to the chains. Pressure also increases the magnitude of $\delta\alpha_a(T)$ at lower temperature as well as T_c, again showing the association of T_c with $\delta\alpha_a(T)$ that has been previously emphasized [4,16]. Moreover, pressure also reduces $\alpha_b(T)$, Fig. 3(b), which signals an increase of the negative enhancement term $\delta\alpha_b(T)$ of the chain contribution. The enhancement $\delta\alpha(T)$ in $\alpha_a(T)$ is unique to high T_c cuprates; it appears to be related to the superconductivity in the CuO_2 sheets [9]. The negative enhancement in $\alpha_b(T)$ looks similar to the enhancement in $\alpha_a(T)$, which indicates that the phenomenon associated with superconductivity in the sheets induces a similar phenomenon in the chains.

The work on single crystals allows us to clarify that the polycrystalline $\alpha(T)$ data [4,17] are due to a combination of $\alpha_a(T)$ and $\alpha_b(T)$. The temperature T_g found by Tallon *et al.* [17], who claimed a relation between T_g and T_s based on the TEP data in their polycrystalline sample, is not present in our $\alpha_a(T)$ and $\alpha_b(T)$ at all. TEP is a basic transport measurement that is very sensitive to the opening of a gap or pseudogap in an electronic spectrum. Our measurements of both resistivity and TEP do not support the influence on transport properties from a spin gap.

Both detwinned $YBa_2Cu_3O_7$ and Y-124 show a strong anisotropy in their transport properties due to the presence of Cu-O chains. These Cu-O chains are coupled via a **c**-axis oxygen to the CuO_2 sheets. On review of the resistivity along the **c** axis [18], all cuprates, except detwinned $YBa_2Cu_3O_7$ and Y-124, show semiconductive behavior of ρ_c from underdoped to optimally doped compositions. However, a detwinned $YBa_2Cu_3O_7$ crystal shows a metallic ρ_c. Correspondingly ρ_a in this crystal changes linearly with temperature, but with a relatively high slope [15]. The same feature is found in ρ_a of Y-124, Fig. 2(a), in the range $100 \leq T \leq 150$ K. Interestingly, R_c shows a change from semiconductive behavior above 170 K to a state with a positive dR_c/dT at lower temperatures. It is likely that the linear dependence of ρ_a in the range $100 \leq T \leq 150$ K is related to a coupling along the **c** axis between the CuO_2 sheets and the Cu-O chains. To be more specific, the linear dependence in ρ_a appears to be related to a dynamic lattice modulation in the Cu-O chains. This modulation has been found recently by neutron diffraction at room temperature for a $YBa_2Cu_3O_{6.93}$ crystal [19], and the same modulation occurs below 170 K in Y-124 [20]. In addition, infrared data [21] show a decreased charge-carrier scattering rate in the CuO_2 sheets below $T^* = T_D$ that correlates with the sharpening of a **c**-axis pseudogap. However, the absence of any influence on α_c at T_D and a reduced ρ_c below T_D suggest an increased charge-carrier mobility rather than a change in the density of states $N(\varepsilon_F)$.

TEP has also been used widely to determine the hole fraction *p*, i.e., the Cu(III)/Cu ratio, in the CuO_2 sheets. Obertelli, Cooper, and Tallon [10] have proposed a "universal plot" between $T_c/T_{c\,\max}$, $\alpha_0 \approx \alpha(300\text{ K})$, and *p* that appears to be applicable to most cuprate systems where only the CuO_2 sheets contribute to T_c and α_0. In underdoped samples, a $dT_c/d\alpha_0 < 0$ corresponds to a T_c that increases with increasing oxidation of the CuO_2 sheets; and for the $YBa_2Cu_4O_8$ structure having a $T_{c\,\max} \approx 90$ K taken from the $Y_{1-y}Ca_yBa_2Cu_4O_8$ system [22], the universal plot gives $dT_c/d\alpha_0 \approx -0.4$ K/(μV/K). Figure 2(b) shows $d\alpha(300\text{ K})/dP$ and the corresponding dT_c/dP from which we obtain $dT_c/d\alpha_0 \approx -7.5$ K/(μV/K), nearly a factor of 2 too large.

To rationalize this discrepancy, we need to consider the effect of any superconductivity induced in the double Cu(1)-O chains. It has been well established that complete Cu(1)-O chains, if coupled via **c**-axis oxygen to the CuO_2 sheets, are involved in the superconductive condensation below T_c [23]. Tallon *et al.* [24] have used μSR to demonstrate that, in underdoped $Y_{1-x}Ca_xBa_2Cu_4O_8$, T_c increases monotonically with the total concentration $n_s(t) = n_s(p) + n_s(c)$ of superconductive pairs in both the sheets and the chains. A $dT_c/d\alpha_0 \approx -7.5$ K/(μV/K) in $YBa_2Cu_4O_8$ suggests that pressure increases T_c not only by transferring electrons from the CuO_2 sheets, which increases $n_s(p)$, but also by increasing $n_s(c)$ in this underdoped sample; T_c reflects $n_s(t)$, and $\alpha_a(300\text{ K})$ can relate only to *p* and hence only to $n_s(p)$ according to the Uemura plot [25]. Since the negative enhancement term in α_b increases with pressure, and this enhancement is associated with the high-T_c phenomenon [9], Fig. 3(b) provides independent evidence for a $dn_s(c)/dP > 0$.

We summarize our conclusions of this paper as follows: (a) Measurements on a Y-124 crystal show a strongly anisotropic resistivity; and a large ratio $(d\ln\rho_a/d\ln a)/(d\ln\rho_b/d\ln b) \approx 10$ has been found, which indicates an unusual sensitivity of the conduction in the CuO_2 sheets to charge density. (b) The temperature dependence of the resistivity ρ_a, TEP α_a, and their behavior under pressure do not support the influence of a spin gap or pseudogap on the transport properties. (c) A large $dT_c/d\alpha(300\text{ K})$ that deviates from the universal plot is due to a pair contribution from the Cu-O chains. (d) A change of slope in ρ_a is correlated to a change in R_c and the formation of a dynamic lattice modulation in the Cu-O chains.

The authors are grateful to the National Science Foundation Grants No. DMR-9528826 (J. B. G.) and No. DMR-91-20000 (B. D.) for financial support.

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[1] J. Karpinski *et al.*, Nature (London) **366**, 660 (1988).
[2] E. Kaldis *et al.*, Physica (Amsterdam) **159C**, 668 (1989).
[3] Y. Yamada *et al.*, Physica (Amsterdam) **173C**, 185 (1991).
[4] J.-S. Zhou and J. B. Goodenough, Phys. Rev. B **53**, R11 976 (1996).
[5] B. Bucher *et al.*, Phys. Rev. Lett. **70**, 2012 (1993).
[6] B. Dabrowski *et al.*, Physica (Amsterdam) **202C**, 271 (1992).
[7] J. J. Scholtz, E. N. van Eenige, R. I. Wijingaarden, and R. Griessen, Phys. Rev. B **45**, 3077 (1992); B. Bucher, J. Karpinski, E. Kaldis, and P. Wachter, Physica (Amsterdam) **157C**, 478 (1989).
[8] A. J. Lowe, S. Regan, and M. A. Howson, Phys. Rev. B **44**, 9757 (1991).
[9] J.-S. Zhou and J. B. Goodenough, Phys. Rev. B **51**, 3104 (1995).
[10] S. D. Obertelli, J. R. Cooper, and J. L. Tallon, Phys. Rev. B **46**, 14 928 (1992).
[11] J.-S. Zhou, J. P. Zhou, J. B. Goodenough, and J. T. McDevitt, Phys. Rev. B **51**, 3250 (1995).
[12] N. Nagoasa and P. A. Lee, Phys. Rev. B **45**, 966 (1992); B. L. Altshler, L. B. Ioffe, and A. J. Millis, Phys. Rev. B **53**, 415 (1996).
[13] R. L. Corey *et al.*, Phys. Rev. B **53**, 5907 (1996).
[14] T. Machi *et al.*, Physica (Amsterdam) **173C**, 32 (1991).
[15] T. A. Friedmann *et al.*, Phys. Rev. B **42**, 6217 (1990).
[16] J.-S. Zhou and J. B. Goodenough, Phys. Rev. Lett. **77**, 151 (1996).
[17] J. L. Tallon *et al.*, Phys. Rev. Lett. **75**, 4114 (1995).
[18] T. Ito *et al.*, Nature (London) **350**, 596 (1991).
[19] H. A. Mook *et al.*, Phys. Rev. Lett. **77**, 370 (1996).
[20] T. R. Sendyka *et al.*, Phys. Rev. B **51**, 6747 (1995).
[21] D. N. Bosov *et al.* (to be published).
[22] T. Migatake *et al.*, Physica (Amsterdam) **167C**, 297 (1990).
[23] D. N. Basov *et al.*, Phys. Rev. Lett. **74**, 598 (1995).
[24] J. L. Tallon *et al.*, Phys. Rev. Lett. **74**, 1008 (1995).
[25] Y. J. Uemura *et al.*, Phys. Rev. Lett. **66**, 2665 (1991).