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Anomalous transport properties in a $YBa_2Cu_4O_8$ crystal

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Resistivity $\rho(T)$ and thermoelectric power $\alpha(T)$ have been measured under hydrostatic pressure on a 1% Ni-doped $YBa_2Cu_4O_8$ crystal grown under 600 bars O_2 pressure. The Ni are shown to substitute predominantly for the chain Cu and to suppress the chain superconductivity. A giant $dT_c/dP = 1.2$ K/kbar and $d\alpha(300\ \mathrm{K})/dP = 0.2\ \mu$V/K kbar are interpreted to signal a reduction of Ni(III) to N(II) in the chains by the application of pressure. The temperature of the transition in $\rho_a(T)$ and $\rho_c(T)$ remains near 170 K independent of significant changes in the charge distribution between chains and bilayers, consistent with a structure-induced transition rather than the opening of a spin gap. [S0163-1829(98)51230-1]

The opening of a spin gap, or pseudogap, below a temperature $T_s > T_c$ has been identified in several copper-oxide superconductors.[1] T_s decreases as T_c increases with increasing hole concentration in the underdoped superconductive CuO_2 sheets, which has fueled speculation that the spin-spin interactions are the driving force for the formation of superconductive Cooper pairs. If this speculation were true, we should expect to find some change in the transport properties at T_s.

Stoichiometric $YBa_2Cu_4O_8$ (Y1248) is an underdoped *p*-type superconductor containing CuO_2-Y-CuO_2 bilayers alternating along the *c* axis with Cu_2O_2 edge-shared double chains. As-grown Y1248 crystals are stoichiometric and naturally detwinned. There is no oxygen loss up to 850 °C, which makes these crystals ideal for obtaining separate transport data for the bilayers (*a*-axis measurements) and the chains plus bilayers (*b*-axis measurements) as well as along the *c* axis. Therefore, the observation[2,3] of a change in slope near 170 K of the *a*-axis resistivity $\rho_a(T)$ in Y1248 is significant. Since similar anomalies have been noted in other underdoped copper-oxide superconductors, it was considered to be a candidate signature of the opening of a spin gap at T_s.[2,4]

In Y1248, as in $YBa_2Cu_3O_{7-\delta}$ (Y123), an overlap of the Cu(III)/Cu(II) redox energies of the chains and bilayers makes the chains a charge reservoir of the bilayers. If the thermoelectric power is obtained as a function of pressure and temperature along the three crystallographic axes, it is possible to monitor the transfer of charge between the chains and bilayers as a function of pressure as well as temperature. We[3] have used this strategy with single-crystal Y1248 to demonstrate that the anomaly in $\rho_a(T)$ near 170 K in this cuprate is not associated with the opening of a spin gap at T_s but, instead, with a maximum in the *c*-axis resistance $R_c(T)$. Most copper-oxide superconductors show only an activated *c*-axis conductivity above T_c, the metallic temperature dependence of $R_c(T)$ observed[3,5] below 170 K in Y1248 is unusual. Sendyka *et al.*[6] have revealed with pulsed-neutron-scattering experiments the formation of fluctuating microdomains in the Cu_2O_2 chains below 170 K and Suter *et al.*[7] have detected enhanced charge fluctuations in both the bilayers and chains around 180 K with NMR and nuclear quadrupole resonance (NQR) spectroscopies on Cu, O, and Y isotopes; the charge fluctuations mark the onset of an electron transfer from the bilayers to the chains. The changes in transport properties at $T_D \approx 170$ K apparently reflect electron coupling to cooperative structural fluctuations that enhance *c*-axis electron transfer rather than the opening of a spin gap.

In this paper, we extend our previous work[3] by reporting transport measurements made under different hydrostatic pressures on a 1% Ni-doped Y1248 crystal that were undertaken to clarify (1) whether the Ni substitutes for chain or bilayer Cu in a crystal grown under 600 bars O_2 pressure, (2) how the nickel atoms in such a crystal influence the charge distribution between chains and bilayers, and (3) whether the anomaly in $\rho_a(T)$ and maximum in $R_c(T)$ are retained in the Ni-doped samples and how the temperature T_D of the anomaly responds to changes in the charge distribution and T_c. In addition, a possible suppression of the superconductivity in the chains, but not in the bilayers, allows us (4) to test further the correlation we have noted[8] between superconductivity and an enhancement below 300 K of the thermoelectric power with a maximum at $T_{\max} \approx 140$ K.

Dopants can influence T_c by changing the charge distribution between the chains and CuO_2 sheets as well as by disrupting the periodic potential in the CuO_2 sheets. In the Y123 and Y1248 crystals, substitution for chain copper has little influence on the periodic potential in the CuO_2 sheets whereas substitution into the sheets suppresses T_c sharply. In general, trivalent cations substitute preferentially into the chain sites and divalent cations into the CuO_2 sheets.[9] Specifically, Ni(II) ions substitute into the bilayers of Y1248 synthesized under ambient pressure.[10] However, oxidation of the Ni(II) to Ni(III) ions under high oxygen pressure can be expected to remove the nickel from the bilayers to the chains. In the absence of high-quality single crystals, previous determinations of a dopant location have used local probes such as Mössbauer spectroscopy.[11] Here we use transport measurements to interrogate the location of the nickel dopant in a high-quality 1% Ni-doped single crystal

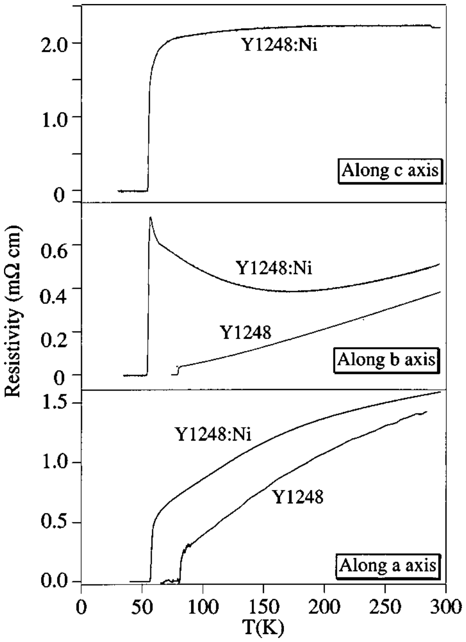

FIG. 1. Resistivity vs temperature along the *a*, *b*, *c* axes of 1% Ni-doped Y1248 compared to that along the *a* and *b* axes in pure Y1248.

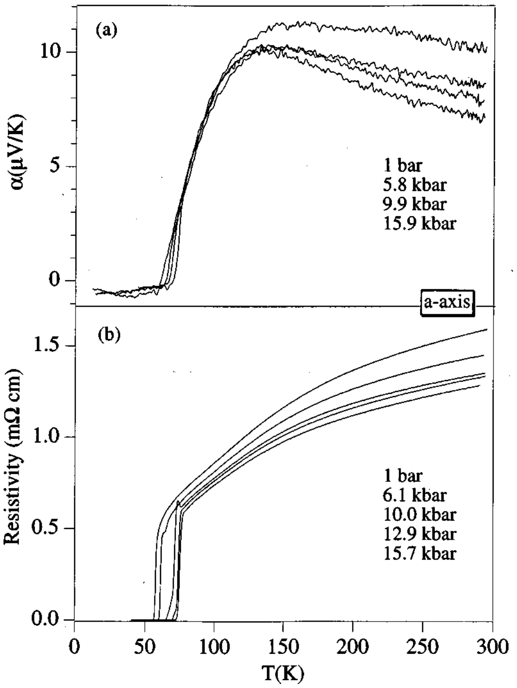

FIG. 2. (a) Thermoelectric power and (b) resistivity vs temperature along the *a* axis of 1% Ni-doped Y1248 under several hydrostatic pressures.

grown in a high-temperature, high-pressure furnace under 600 bars O_2 pressure.[12] $Ln\mathrm{NiO}_3$ perovskites (Ln = rare-earth atom) containing Ni(III) ions have been synthesized under the same oxygen pressure.[13] ac magnetic-susceptibility measurements showed a nonfilamentary superconductivity with a $T_c = 57$ K, which is to be compared with $T_c = 81$ K in a pure Y1248 crystal.[3]

The size of the crystal used in our transport measurements was $0.4\times0.3\times0.1\ \mathrm{mm}^3$. The *b* axis was in the direction of the long axis of the crystal; the *c* axis was along the short direction. Four gold spots were deposited on the corners of the crystal plate before copper wires were attached with silver epoxy. All the transport measurements reported were performed on the same crystal; the basic features of the data were reproducible on other crystals. We define T_0 as the temperature below which no voltage is resolvable with a nanovoltmeter.

The pressure experiments were carried out in a CuBe pressure cell as reported elsewhere.[14] The pressure inside the chamber was monitored with a coil of manganine wire. The contribution from the Cu leads was subtracted from all the $\alpha(T)$ data.

Figure 1 compares the resistivities $\rho_a(T)$ and $\rho_b(T)$ at ambient pressure with those reported[3] for pure Y1248. The two $\rho_a(T)$ curves are similar, each showing a change of slope near 170 K. The Ni-doped sample has a somewhat higher resistivity and lower T_c, indicative of fewer holes in the underdoped bilayers; there is no evidence of a stronger scattering of charge carriers by nickel atoms in the bilayers. On the other hand, the *b*-axis resistivity $\rho_b(T)$ shows an important change. Whereas $\rho_b(T)$ for the pure Y1248 crystal shows no change of slope on cooling through 170 K, the $\rho_b(T)$ for the nickel-doped sample is not only higher but also shows a minimum near 170 K. In the pure crystal, a higher conductivity in the chains masks the anomaly in the bilayer contribution to $\rho_b(T)$. In the Ni-doped samples, the $\rho_b(T)$ curve clearly shows a progressive loss of chain charge carriers and/or their mobility on cooling below 170 K, and we can unambiguously conclude that the nickel atoms are located predominantly in the chains as Ni(III) ions. Since retention of oxygen stoichiometry is a basic feature of the Y1248 structure, the introduction of a higher-valence Ni(III) ion into the $\mathrm{Cu}_2\mathrm{O}_2$ chains should increase the net electron transfer from the chains to the bilayers, thus lowering T_c by reducing further the oxidation state of the underdoped bilayers. This deduction is also consistent with an increase with Ni doping in the *a*-axis thermoelectric power α_a at 300 K; see Fig. 2 and discussion below. The modest decrease in T_c at atmospheric pressure from 81 to 57 K with 1% Ni doping appears to reflect primarily the greater underdoping of the bilayers and suppression of any chain superconductivity as is discussed below.

From Fig. 1, the change in slope of $\rho_a(T)$ for the Ni-doped sample occurs over a somewhat broader temperature range than in the pure crystal, but it remains centered near $160 \leq T_D \leq 180$ K. Independence of T_D on the charge distribution would be characteristic of a lattice-driven anomaly, but not of the opening up of a spin gap.

The thermoelectric power along the *b* axis (Fig. 3) contains a negative contribution from the chains and a positive contribution from the bilayers, but the higher conductivity of the chains (Fig. 1) makes the negative contribution dominant.[3] Within a narrow range of temperature above T_c, the *a*- and *b*-axis resistivities are nearly equal. The thermoelectric power α_a, however, is negligible at these temperatures. Therefore the negative contribution dominates below room temperature. A negative chain contribution to $\alpha(T)$ has been demonstrated in Y123.[15] Whereas $\alpha_b(T)$ for pure Y1248 has an important negative enhancement term with a maximum near $T_{\mathrm{max}} \approx 140$ K,[3] this maximum is largely sup-

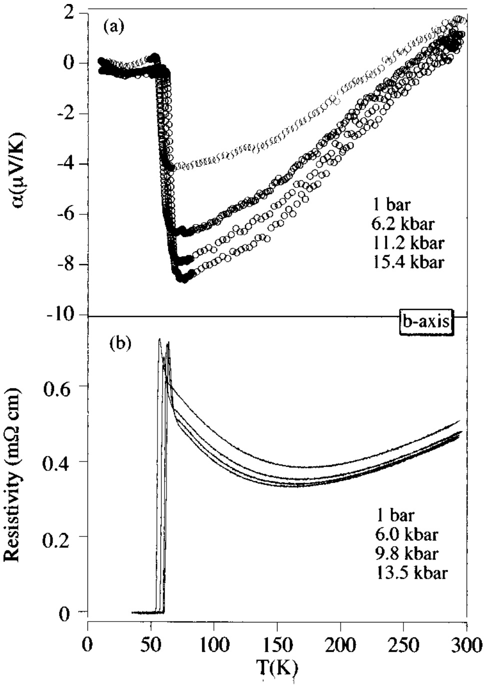

FIG. 3. Same as Fig. 2 along the *b* axis.

pressed in the Ni-doped crystal. We have shown[8] that an enhancement of $\alpha(T)$ with a maximum near 140 K is a signature of superconductivity, and indeed Fig. 2(a) shows a positive enhancement peak for the bilayers that becomes more pronounced as T_c increases with pressure. This enhancement is essentially confined to the temperature range $T<300$ K; above 300 K we find a nearly temperature-independent $\alpha(T)$ so that α(300 K) gives a measure of the relative concentration of mobile holes in the bilayers. In fully oxidized Y123, the chains have been shown to be superconductive,[16] and a corresponding negative enhancement in $\alpha_b(T)$ has been found.[15] Since the chain-only structure of Sr_2CuO_3 does not become superconductive on doping into the metallic state,[17] the chain superconductivity in Y123 appears to be induced by coupling to the bilayers. A similar correlation should be applicable to Y1248, and indeed we have found a negative enhancement in $\alpha_b(T)$ in pure Y1248.[3] In the Ni-doped crystal, the lack of a similar negative enhancement of $\alpha_b(T)$ leads us to conclude there is a suppression of the chain superconductivity by the Ni atoms.

Figures. 2(b) and 3(b) show that the pressure dependence of $\rho_a(T)$ is dramatic, particularly above 170 K, whereas $\rho_b(T)$ is relatively insensitive to pressure. On the other hand, the temperature T_D of the anomaly is essentially unchanged. This behavior is similar to that found for pure Y1248.[3]

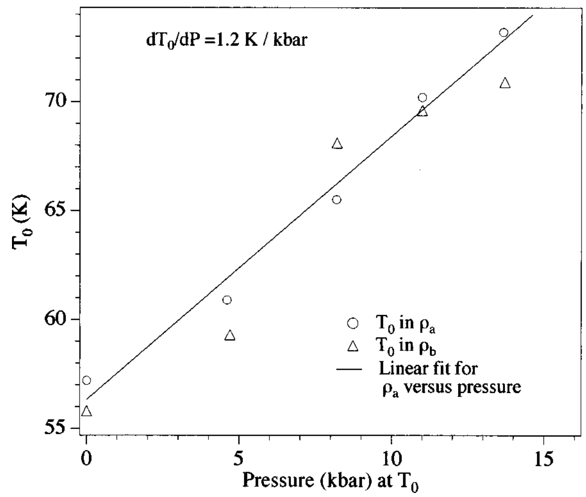

FIG. 4. Pressure dependence of T_0 from $\rho_a(T)$ and $\rho_b(T)$ data.

In Fig. 4, the increase in the superconductive transition temperature with pressure, $dT_0/dP\approx 1.2$ K/kbar, is the largest ever reported. A $dT_0/dP\approx 0.44$ K/kbar for 123 is considered to be unusually high and has been attributed to a pressure-induced electron transfer between the chains and the bilayers in that structure.[18] We have reported a $dT_0/dP \approx 0.58$ K/kbar for pure Y1248 and have confirmed, with thermoelectric-power measurements, that the high value is due to a pressure-induced transfer of electrons from the bilayers to the chains.[3] This model should also be applicable to the Ni-doped Y1248 crystal, and the pressure coefficient $d\alpha(300\text{ K})/dP\approx 0.2$ μV/K kbar seen in Fig. 2(a) confirms an exceptionally large pressure-induced charge transfer. A smaller $d\alpha(300\text{ K})/dP\approx 0.07$ μV/K kbar found for pure Y1248 is consistent with its smaller dT_0/dP. Pressure stabilizes the redox energies of the chains relative to those of the bilayers, and the exceptionally high pressure-induced electron transfer from bilayers to chains in the Ni-doped Y1248 implies that the Ni(III) ions of the chains are reduced to Ni(II) ions by the application of pressure. At low temperatures, the nickel atoms are not mobile, and the pressure-induced reduction of the Ni(III) is reversible. From the square-coplanar configuration of the chain sites, we would expect the Ni(II) ions in the chains to be in their low-spin, diamagnetic state. Alternatively, the large pressure coefficient might be attributed to a conventional charge transfer if there is also a recovery under pressure of superconductivity in the chains. However, the shapes of $\alpha_b(T)$ and $\rho_b(T)$ in Fig. 3 change little under pressure, which means there is no evidence of a recovery of superconductivity in the chains.

In summary, measurements of $\rho(T)$ and $\alpha(T)$ on a Ni-doped Y1248 crystal under different hydrostatic pressures have allowed us to draw the following conclusions: (1) In a 1% Ni-doped Y1248 crystal prepared at 600 bars O_2 pressure, Ni substitutes for chain Cu as low-spin Ni(III). The Ni atoms suppress the bilayer-induced superconductivity in the chains and, below 170 K, introduce a semiconductive temperature dependence in the chain resistivity $\rho_b(T)$. (2) The presence of Ni(III) in the chain sites lowers the oxidation state of the bilayers. Since the bilayers are underdoped, lowering of their oxidation state lowers the superconductive transition temperature T_0, and the lowering of T_c from 81 K in pure Y1248 to 57 K in 1% Ni-doped Y1248 is due in large part to the lower oxidation state of the bilayers and suppression of the chain superconductivity. Pressure induces an exceptionally large electron transfer from the bilayers to the chains indicative of a reduction of low-spin Ni(III) to Ni(II), and a giant $dT_0/dP\approx 1.2$ K/kbar demonstrates the sensitivity of T_0 to the oxidation state of the bilayers even in the presence of Ni atoms in the chains that suppress the bilayer-induced chain superconductivity. (3) The anomaly in $\rho_a(T)$ is broadened by Ni doping; but unlike T_0, the center of the temperature interval over which it occurs remains essentially independent of the charge distribution between chains and bilayers. This behavior is consistent with a structure-induced transition and not with the opening of a spin gap. (4) The observation of an enhancement of $\alpha_a(T)$ below 300 K that has a maximum at $T_{\max}\approx 140$ K and increases with the superconductive transition temperature provides one more example of the association of this enhancement with high-temperature superconductivity in the copper oxides. The observation that this enhancement is found for the chains in $\alpha_b(T)$ of pure Y1248 but is suppressed in the Ni-doped Y1248 is consistent with location of the Ni atoms in the chains where they suppress the chain superconductivity induced, in pure Y1248, by the bilayer superconductivity. (5) Finally, Fig. 1 shows that in the Ni-doped sample the metallic temperature dependence of $R_c(T)$ below $T_D \approx 170$ K is retained, but that of $\rho_b(T)$ is not, which indicates that the c-axis resistivity is only weakly coupled, if at all, to the conductivity of the chains.

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[1] R. L. Corey *et al.*, Phys. Rev. B **53**, 5907 (1996), for example.

[2] B. Bucher *et al.*, Phys. Rev. Lett. **70**, 2012 (1993).

[3] J.-S. Zhou, J. B. Goodenough, B. Dabrowski, and K. Rogacki, Phys. Rev. Lett. **77**, 4253 (1996).

[4] J. L. Tallon *et al.*, Phys. Rev. Lett. **75**, 4114 (1995).

[5] N. E. Hussey, K. Nozawa, H. Takagi, S. Adachi, and K. Tanabe, Phys. Rev. B **56**, R11 423 (1997).

[6] T. R. Sendyka, W. Dmowski, T. Egami, N. Seiji, H. Yamauchi, and S. Tanaka, Phys. Rev. B **51**, 6747 (1995).

[7] A. Suter, M. Mali, J. Roos, D. Brinkmann, J. Karpinski, and E. Kaldis, Phys. Rev. B **56**, 5542 (1997).

[8] J.-S. Zhou and J. B. Goodenough, Phys. Rev. B **51**, 3104 (1995); J.-S. Zhou, J. B. Goodenough, and G. I. Bersuker, J. Supercond. **8**, 541 (1995).

[9] Y. Xu *et al.*, Physica C **169**, 205 (1990), for example in Y123; N. Watanbe, N. Kooshizuga, N. Seiji, and H. Yamaushi, *ibid.* **234**, 361 (1994), for example in Y1248.

[10] M. Verma and V. S. Tomar, Physica C **272**, 335 (1996).

[11] M. G. Smith, J. B. Goodenough, R. D. Taylor, J. J. Neumeier, and J. O. Willis, Physica C **222**, 159 (1994), for example.

[12] B. Dabrowski, K. Rogacki, C. Zheng, and D. G. Hinks, Physica C **291**, 287 (1997).

[13] B. Dabrowski (unpublished).

[14] J.-S. Zhou and J. B. Goodenough, Phys. Rev. B **54**, 13 393 (1996).

[15] J.-S. Zhou, J.-P. Zhou, J. B. Goodenough, and J. T. McDevitt, Phys. Rev. B **51**, 3250 (1995).

[16] N. Klein, N. Tellman, H. Schulz, K. Urban, S. P. Wolf, and V. Z. Kresin, Phys. Rev. Lett. **77**, 3355 (1993).

[17] W. Archibald, J.-S. Zhou, and J. B. Goodenough, Phys. Rev. B **52**, 16 101 (1995).

[18] C. C. Almasan *et al.*, Phys. Rev. Lett. **69**, 680 (1992).