RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 51, NUMBER 21 1 JUNE 1995-I

Transport properties of zinc-doped $YBa_2Cu_3O_{7-\delta}$ thin films

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(Received 27 January 1995)

We report the results of transport measurements on single-crystal $YBa_2(Cu_{1-x}Zn_x)_3O_{7-\delta}$ thin films grown by laser ablation. Matthiessen's rule is obeyed as a function of x at optimum doping ($\delta \sim 0.05$), but is violated in underdoped samples, where there is evidence from the resistivity that zinc fills in the pseudogap that is observed for samples with $x=0$, $\delta > 0.2$. As x and δ are increased, T_c drops rapidly, and a superconductor-insulator transition is observed at a sheet resistance of approximately $h/(2e)^2$ per copper-oxygen bilayer, for various different combinations of x and δ.

The effects of oxygen depletion on $YBa_2Cu_3O_{7-\delta}$ are well documented.[1] As the material is underdoped by oxygen removal, the resistivity (ρ) develops significant downward curvature below a temperature T^* which is dependent on the doping level. The values of T^* correspond closely to those obtained by other measurements[2–5] which are thought to probe the opening of a pseudogap in the spin excitation spectrum. Since it is unlikely that the number of carriers increases below T^*, it appears that this "spin gap" reduces the in-plane scattering rate. Extension of this type of study to Zn-doped cuprate superconductors is of interest because Zn substitutes for the in-plane copper atoms, leading to an enhancement of the in-plane scattering rate and a rapid drop of T_c.[6–9] So far, most transport studies of the effects of Zn doping have concentrated on fully oxygenated material, in which T_c is reduced by approximately 10 K per at. % of Zn. Recently, there have been several reports based on measurements of the specific heat,[10] inelastic neutron scattering,[11] NMR,[12] ESR,[4] and the thermoelectric power[13] that the substitution of Zn into oxygen depleted $YBa_2Cu_3O_{7-\delta}$ restores some of the low-energy excitations, and so fills in the spin gap.

In this paper we summarize a study of the transport properties of $YBa_2(Cu_{1-x}Zn_x)_3O_{7-\delta}$ thin films with $0<x<0.07$ and $0.05<\delta<0.67$. Matthiessen's rule is followed quite well as a function of x in the fully oxygenated material, and for $0<x<0.03$ and $0.23<\delta<0.32$, there is evidence that Zn substitution fills the spin gap. As x and δ are increased above these values, there is a superconductor to insulator transition at a sheet resistance of approximately $h/(2e)^2$ per CuO_2 bilayer.

The films were grown on $SrTiO_3$ substrates by laser ablation from sintered targets of $YBa_2(Cu_{1-x}Zn_x)_3O_{7-\delta}$, using deposition conditions and deoxygenation procedures outlined in Refs. 1 and 14. They were patterned photolithographically into Hall bars with two pairs of contacts for measuring either the resistivity or Hall effect. Film stoichiometry was determined by electron probe microanalysis (EPMA). Low accelerating voltages (<6.5 keV) were used to ensure that the electrons were confined to the films.[15] All elements were studied, using single-crystal $YBa_2Cu_3O_{7-\delta}$ and pure Zn as calibration standards, and the Cu $L\alpha$ and Zn $L\alpha$ x-ray lines were resolved by using wavelength dispersive x-ray spectrometers.

Film thickness determination is important for a study of this kind, and we also used the electron probe for this. The accelerating voltage was raised until there was significant penetration to the substrate, and the thickness was calculated from the relative emission intensity of the Y $L\alpha$ and Sr $L\alpha$ x-ray lines from the film and substrate, respectively. We estimate the absolute thickness error as 10–15 %, but the precision for film to film changes is better than 1%. This precision is considerably better than we could achieve using profilometry. The transport measurements were made using standard ac methods.

Resistivity measurements on five fully oxygenated films are shown in Fig. 1. The temperature-dependent part of ρ has a very similar slope below 150 K for all x, but shows deviations from this at higher temperatures. Overall, Matthiessen's rule is obeyed fairly well.[7,8] The extrapolated residual resistivity (ρ_{res}) depends linearly on the Zn concentration x (inset), with a slope of 22 $\mu\Omega$ cm/at. % Zn or a sheet resistance of 250 Ω/at. % Zn in each CuO_2 layer. A two-dimensional (2D) scattering analysis[8,16] shows that a phase shift of $\pi/2$ in

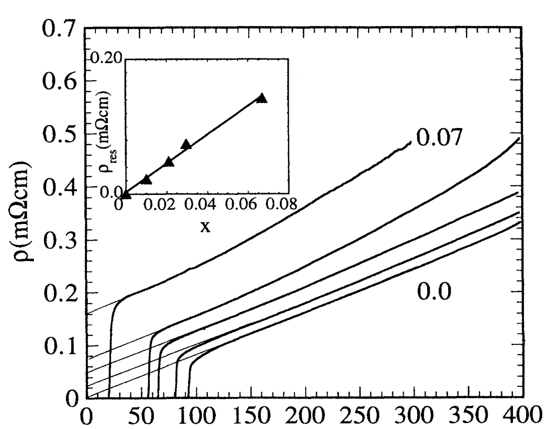

FIG. 1. The resistivity of a series of $YBa_2(Cu_{1-x}Zn_x)_3O_{6.95}$ thin films with $x=0.0$, 0.01, 0.02, 0.03, and 0.07. The extrapolation used to define the residual resistivity is shown by the faint lines. Inset: The residual resistivity shown as a function of x.

the s channel gives a sheet resistance of 143 Ω/at. % Zn for a large Fermi surface ($k_F \sim 0.7$ Å^{-1} or a hole concentration, $n \sim 1.15$/Cu) and 1100 Ω/at. % Zn for a small one ($k_F \sim 0.25$ Å^{-1} or $n \sim 0.15$/Cu). In 2D, $\pi/2$ phase shifts in higher-order channels (e.g. p, f, etc.) give sheet resistances which are a factor of 2 larger.[17] Thus for $\delta = 0.05$ the residual resistivity observed experimentally corresponds approximately to that expected for a large Fermi surface and strong scattering (near the unitarity limit) in the d channel. In contrast, for a small Fermi surface the scattering would be well below the unitarity limit.

For higher-δ values the residual resistivity values are much larger (e.g., ~ 80 $\mu\Omega$ cm/at. % Zn for $\delta = 0.3$). This will be discussed in a more detailed paper, as will Hall data for the same samples. For $\delta = 0.05$ the behavior of the inverse Hall angle ($\cot\Theta_H$) is in close agreement with Ref. 8, but the temperature dependence of R_H is somewhat different. In our work R_H is essentially independent of x (for $0 < x < 0.03$) above 200 K.

The results of a series of deoxygenations of films with $x = 0.01$, 0.02, and 0.03 are shown in Fig. 2. Deoxygenation of pure $YBa_2Cu_3O_{7-\delta}$ leads to a depression of T_c with very little increase in ρ_{res},[1] but the addition of Zn leads to qualitatively different behavior. As x is increased, T_c drops rapidly as a function of δ, and for T_c below 50 K ρ_{res} rises rapidly. Also, the anomalous curvature in the resistivity of the high-δ samples which has been associated with the opening of the spin gap is suppressed as x is increased. For $x = 0$ (Ref. 1) and 0.01 [Fig. 2(a)] $d\rho/dT$ increases with δ even at high temperatures, where ρ is linear in T, so Matthiessen's rule is not obeyed. Surprisingly, there is a greater tendency to follow Matthiessen's rule with increasing δ in the $x = 0.03$ [Fig. 2(c)] and 0.07 [Fig. 4(c)] samples.

The effects of Zn doping on the "pseudogap" feature in ρ at intermediate δ are more clearly seen in Fig. 3(a), in which ρ is shown as a function of x at $\delta = 0.23$. Clearly, Matthiessen's rule is not obeyed in this underdoped sample, in contrast to the optimally doped case ($\delta = 0.05$, Fig. 1 and Refs. 7 and 8). In common with previous studies on samples with $x = 0$,[1] we associate a drop in ρ below the extrapolation of its high-temperature linear T dependence with a reduction in scattering due to the opening of the pseudogap. The temperature T^* at which the pseudogap opens is defined as the highest temperature at which the deviation from linearity occurs, and is seen to be essentially independent of x, in agreement with Refs. 4 and 10–13. For temperatures below T^*, however, the deviation from the linear extrapolation decreases as x increases, suggesting that the additional conductivity contribution from the opening of the pseudogap also decreases with increasing x. This is shown more explicitly in Fig. 3(b), in which ρ_{res} has been subtracted, and the data have been divided by αT, where α is the slope of the linear region.

The rise of ρ_{res} with δ in Fig. 2 and the apparent localization in the $x = 0.03$ sample in Fig. 3(a) could, in principle, be due to changes in the quality of the grain boundaries as the deoxygenation is performed. Any changes that occur are certainly reversible, as the films could be cycled to and from optimum doping without a significant change in the resistivity. The data shown in Fig. 4 give further evidence that the rise in ρ_{res} is intrinsic. If oxygen depletion is continued until

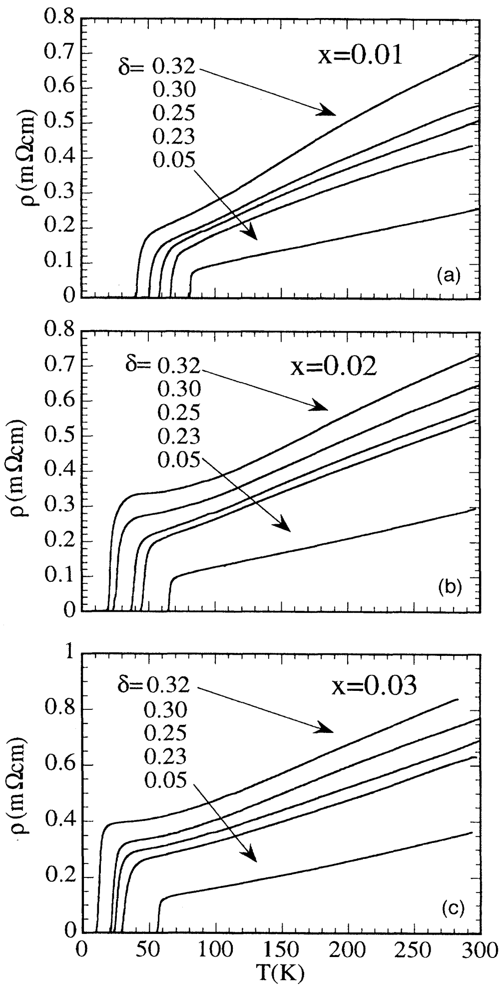

FIG. 2. The resistivity of three films with $x = 0.01$, 0.02, and 0.03, respectively, for a series of δ values.

superconductivity is destroyed, all the films make a superconductor to insulator transition at approximately the same resistivity. This low-temperature behavior has been carefully studied in ultrathin Bi films,[18] in which it occurs as a sheet resistance of approximately $h/(2e)^2$. This observation has been accounted for in terms of pair localization in all two-dimensional superconductors.[19] We see the transition at a value which is independent of the combination of x and δ that is used, giving confidence that we are observing a universal phenomenon, but the sheet resistance is close to $h/(2e)^2$ per formula unit, or per CuO_2 *bilayer.* A similar observation was made by Mandrus *et al.*,[20] who studied $Bi_2Sr_2(Ca_{1-x}Y_x)Cu_2O_8$ single crystals, which also have two CuO_2 planes per formula unit. In single-layer materials such as $Bi_2Sr_2CuO_6$ (Ref. 21) or $La_{2-x}Sr_xCuO_4$,[22] the value appears to be close to $h/(2e)^2$ per CuO_2 plane.

The coupling between the constituent planes of the bilayers in $YBa_2Cu_3O_{7-\delta}$ is difficult to estimate experimentally, as most measures of the anisotropy are sensitive to the larger separation between the bilayers. So it is unclear whether the observation of the transition at $h/(2e)^2$ per bilayer is simply due to a much stronger coupling between the constituent

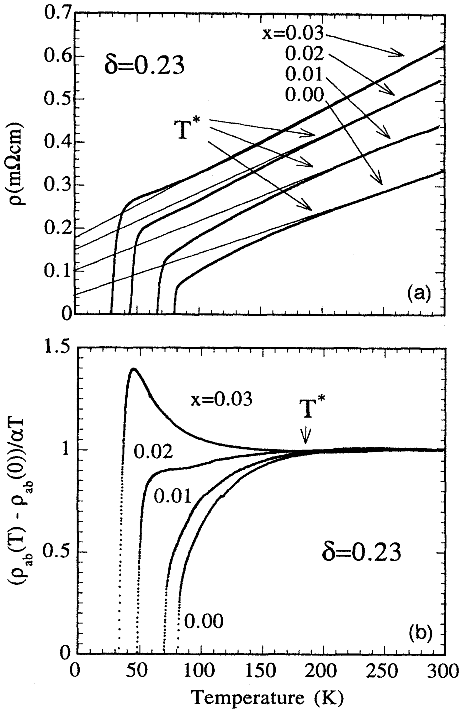

FIG. 3. (a) The x dependence of the resistivity of films for which $\delta=0.23$. The pronounced dip below linear resistivity seen for the $x=0$ sample disappears as x is increased. (b) The inelastic part of ρ normalized to the slope of the linear part plotted against temperature for the same samples.

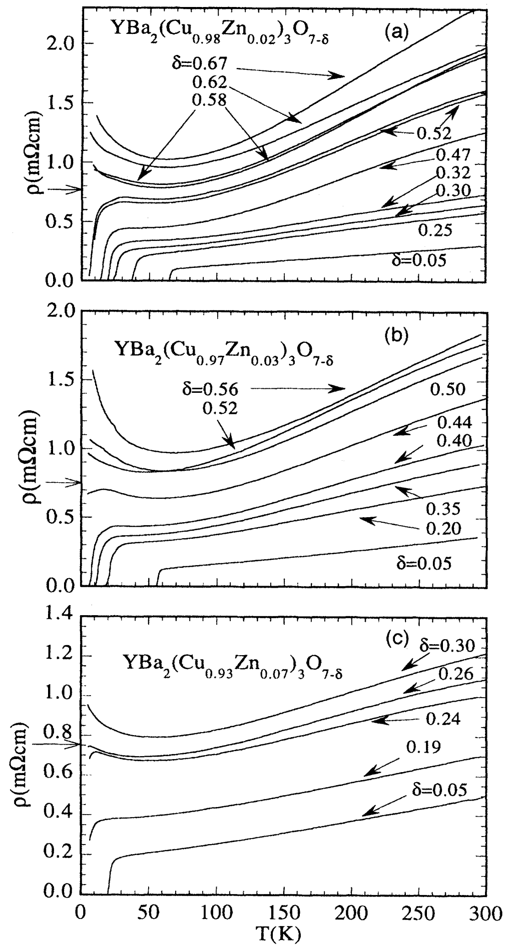

FIG. 4. The superconductor-insulator transition occurs at a similar value of resistivity even if it is induced by three different combinations of x and δ.

planes, or whether it is connected with a fundamental property of pairing in the bilayer cuprates.

Another question concerns the mechanism of the localization. Weak localization has been identified in $Bi_2Sr_2CuO_6$ by Jing *et al.* on the basis of negative transverse magnetoresistance (MR) in the localization regime.[23] We observe only a positive transverse MR in fields up to 7 T for a fully localized $x=0.03$, $\delta=0.56$ sample down to temperatures as low as 3.5 K, even though ρ increases as $-\ln T$ below 12 K, so our data are not really consistent with weak localization. In Ref. 23 weak localization occurs for a nonsuperconducting sample whose sheet resistance is less than 1.5 kΩ per CuO_2 layer, so the mechanism may well be different from that responsible for the localization here and in Refs. 20–22, where the sheet resistance is much higher.

In conclusion, we have studied the resistivity of $YBa_2(Cu_{1-x}Zn_x)_3O_{7-\delta}$ over a wide range of x and δ, and have shown that Matthiessen's rule is obeyed well at $\delta\sim 0$, but is violated at other values of δ. There is also evidence that Zn substitution fills in the pseudogap that occurs in underdoped $YBa_2Cu_3O_{7-\delta}$. As T_c is lowered by a combination of Zn doping and oxygen depletion, superconductivity is destroyed at a universal value of the sheet resistance for various combinations of x and δ, but this corresponds to $h/(2e)^2$ per CuO_2 bilayer, for reasons which are not yet entirely understood.

We are grateful to J. W. Loram, S. Uchida, T. Xiang, and J. M. Wheatley for useful discussions, and to S. Uchida for showing us data prior to publication. K. Scott and E. Fung made significant contributions to the early part of the project. One of us (A.P.M.) gratefully acknowledges the support of the Royal Society.

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[1] For example, J. M. Harris, Y. F. Yang, and N. P. Ong, Phys. Rev. B **46**, 14 293 (1992); T. Ito, K. Takenaka, and S. Uchida, Phys. Rev. Lett. **70**, 3995 (1993); A. Carrington *et al.*, Phys. Rev. B **48**, 13 051 (1993).
[2] J. Rossat-Mignod *et al.*, Physica C **185-189**, 86 (1991).
[3] H. Alloul *et al.*, Phys. Rev. Lett. **67**, 3140 (1991).
[4] A. Janossy *et al.*, Phys. Rev. B **50**, 3442 (1994).
[5] J. W. Loram *et al.*, Phys. Rev. Lett. **71**, 1740 (1993).
[6] Gang Xiao *et al.*, Phys. Rev. Lett. **60**, 1446 (1988).
[7] J. R. Cooper *et al.*, Supercond. Sci. Technol. **4**, S277 (1991).

[8] T. R. Chien, Z. Z. Wang, and N. P. Ong, Phys. Rev. Lett. **67**, 2088 (1991).
[9] C. Kendziora *et al.*, Phys. Rev. B **46**, 14 297 (1992).
[10] J. W. Loram *et al.*, Proc. M^2S-HTSC IV [Physica C **235-240**, 134 (1994)].
[11] K. Kakurai *et al.*, Phys. Rev. B **46**, 14 928 (1993).
[12] A. V. Mahajan *et al.*, Phys. Rev. Lett. **72**, 3100 (1994).
[13] J. R. Cooper *et al.* (unpublished).
[14] D. J. C. Walker, Ph.D. thesis, University of Cambridge, 1994.
[15] A. P. Mackenzie, Rep. Prog. Phys. **56**, 557 (1993).
[16] S. Zagoulaev *et al.*, Physica C **235-240** (1994); (unpublished).
[17] T. Xiang and J. M. Wheatley, Phys. Rev. B **51**, 11 721 (1995).
[18] D. B. Haviland, Y. Liu, and A. M. Goldman, Phys. Rev. Lett. **62**, 2180 (1989).
[19] T. Pang, Phys. Rev. Lett. **62**, 2176 (1989); M. P. A. Fisher, G. Grinstein, and S. M. Girvin, *ibid.* **64**, 587 (1990).
[20] D. Mandrus *et al.*, Phys. Rev. B **44**, 2418 (1991).
[21] S. D. Hughes *et al.*, Physica C **185-189**, 1243 (1991).
[22] S. Uchida (private communication).
[23] T. W. Jing *et al.*, Phys. Rev. Lett. **67**, 761 (1991).