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Effect of Zn doping on charge transport in $YBa_2Cu_3O_{7-y}$

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The resistivity and the in-plane Hall coefficient are investigated on Zn-doped $YBa_2Cu_3O_{7-y}$ single crystals with emphasis on the underdoped spin-gap phase ($y \sim 0.37$) where a correlation between charge transport and spin dynamics is clearly seen. The doped Zn acts as a strong potential scatterer on one hand, and induces a local spin magnetic moment on the other even when the charge carriers are not localized. It is found that the characteristic temperature in these transport coefficients, which indicates that a spin gap starts to open, do not change with Zn doping in contrast to a radical depression of the superconducting transition temperature.

The mechanism of charge transport in the normal state has been one of the fundamental problems of high-T_c superconductor.[1] Recently, an intimate relationship between charge dynamics of doped holes and spin excitations in the CuO_2 plane has been strongly suggested by the transport[2,3] and optical experiments[4] on underdoped $YBa_2Cu_3O_{7-y}$ (Y123) and $YBa_2Cu_4O_8$ (Y124). For the underdoped Y123 (Ref. 2) and Y124,[3] the in-plane resistivity (ρ_a) deviates from the T-linear behavior and the Hall coefficient (R_H) from the $1/T$ one below a certain temperature T^* well above T_c, indicating a suppression of carrier scattering at low temperatures. NMR experiments on these compounds show that the Knight shift (ΔK) decreases with decreasing temperature, and the relaxation rate $(T_1T)^{-1}$ on Cu site [Cu(2)] in the CuO_2 plane is reduced with respect to a Curie-Weiss law, forming a peak at a temperature below T^*.[5] The NMR results are suggestive of opening of a gap (or a pseudogap) in the spin excitation spectrum—so-called *spin gap*—which has been confirmed by the recent neutron experiments.[6] Surprisingly, the out-of-plane (c-axis) optical conductivity spectrum for the underdoped Y123 (Ref. 4) and Y124 (Ref. 7)compound displays the development of a pseudogap below T^*—the optical conductivity in the low-frequency region is progressively suppressed with lowering temperature in the normal state—which appears to be associated with the opening of the spin (pseudo) gap and responsible for the semiconducting T dependence of the c-axis resistivity.[8]

As is well known and is still debated, nonmagnetic Zn substitution for Cu(2) in the high-T_c cuprates radically suppresses T_c.[9] Only a few percent of the Zn substitution completely suppresses superconductivity and makes the compound insulating at low temperatures. ^{89}Y NMR measurements on the Zn-doped Y123 have given an evidence at the microscopic level that the Zn doping creates in-plane disorder without affecting the hole density.[10] However, the NMR as well as μSR studies[11,12] have revealed an interesting change in the magnetic properties of the CuO_2 planes. The Zn doping in the underdoped regime induces local magnetic moments, possibly associated with Cu(2) spins, and when the superconductivity disappears, the local moments freeze at low temperatures, creating a spin-glass-like disordered magnetic state.[12] In this case the pseudogap in the spin excitation spectrum seems to be destroyed as also suggested by the recent NMR experiments on Zn-doped Y124.[13] Since the magnetism and the charge transport in the CuO_2 plane arise from a strongly hybridized state between Cu($3d$) and O($2p$) [Cu($3d$) spins and O($2p$) holes are never decoupled],[14] a change in the magnetic properties should accompany the change in charge dynamics. Therefore, the study of Zn-doping effect on the transport properties will yield a unique opportunity to get deeper insight into the interplay between charge and spin in high-T_c superconductors.

We present in this paper the results of transport properties measured on the Zn-doped Y123 single crystals [$YBa_2(Cu_{1-z}Zn_z)_3O_{7-y}$] with optimum ($y=0.07$, $T_c=92$ K) and underdoped ($y=0.37$, $T_c \sim 60$ K) oxygen content. Single crystals of Zn-doped Y123 were grown by CuO-BaO self-flux method using a Y_2O_3 crucible to avoid contamination from the crucible. This is crucial for the present experiments, as we are concerned with the Zn doping level of 1%. The oxygen concentration was controlled by annealing the crystals at 600 °C for 12 hours in a sealed quartz tube together with Y123 powders which had a prescribed oxygen concentration.[2] Then we cooled them slowly to promote oxygen ordering and to ascertain the same oxygen concentration as that of the powders. The crystals grown and annealed by these processes have high quality and homogeneity which are evidenced by a sharp superconducting transition as well as by the lowest normal-state resistivities among so far reported values, and thus allow for a systematic and quantitative study. The crystals of $y=0.07$ were detwinned to measure the pure contribution (ρ_a) from the CuO_2 planes.

The Zn content was examined by electron-probe-micro-analysis (EPMA) and we did not find inhomogenity in the Zn concentration within the accuracy of the instrument. Furthermore, we checked the sample dependence of ρ_{ab} using several crystals grown and annealed at the same time. The variation of T_c among different crystals was within 1 K and that of ρ_{ab} was within 5%. A rather sharp superconducting transition even for Zn-doped crystals and systematic increase in the normal-state resistivities with z as shown below provide further evidence for homogeneous distribution of Zn. The measurements of R_H and ρ_{ab} were performed using conventional six-probe method, and the interplane resistivity (ρ_c) was measured using tetragonal-symmetry Montgomery method.[15]

Figure 1 shows the temperature dependence of ρ_{ab} for

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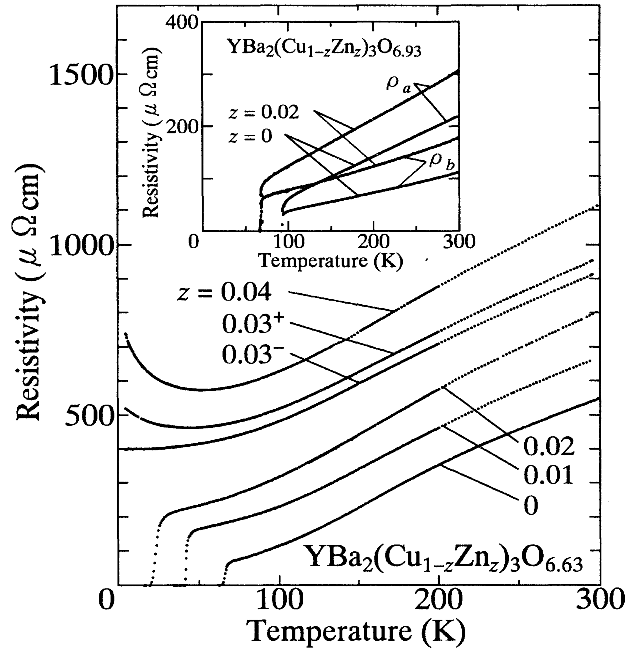

FIG. 1. Temperature dependence of the in-plane resistivity for $YBa_2(Cu_{1-z}Zn_z)_3O_{7-y}$ with $y = 0.37$ and z ranging from 0 to 0.04. The inset shows the temperature dependence of the resistivity both in a and b direction measured on twin-free single crystals of fully oxygenated ($y \sim 0.07$) crystals with $z = 0$ and $z = 0.02$.

Zn-doped Y123 microtwinned single crystals with oxygen deficiency $y = 0.37$. As far as the T dependence is concerned, ρ_{ab} is basically the same as ρ_a which includes the contribution only from the CuO_2 planes since the chain contribution should be very small due to oxygen disorder in the chains.[8] For both optimal and underdoped compounds, a temperature independent residual resistivity component (ρ_0) adds to ρ_{ab} of Zn-free crystal with increasing Zn concentration.

Figure 1 demonstrates that, for the oxygen-reduced Y123, Zn doping induces a superconductor-insulator transition at $z_c \sim 0.03$. The critical resistivity is ~ 400 $\mu\Omega$ cm which corresponds to ~ 6.8 k$\Omega/\square$ *per* CuO_2 *plane* and is close to the universal value $h/4e^2 = 6.45$ k$\Omega/\square$. The critical resistance in the two-dimensional system which separate the superconducting regime from insulating one have attracted much interest. Haviland, Liu, and Goldman[16] showed that for amorphous Bi thin films the transition takes place at the sheet resistance equal to the universal value. It has been reported that for high-T_c films, $DyBa_2Cu_3O_{7-y}$ and $Nd_{2-x}Ce_xCuO_{4-\delta}$, the transition takes place at ~ 6 k$\Omega/\square$ (Ref. 17) and 8~9 k$\Omega/\square$,[18] respectively.

The most notable fact in Fig. 1 is that the Zn doping induces a T-independent term in ρ_{ab} without changing the T-dependent term. This is the case also with fully oxygenated Y123 (Ref. 19) as shown in the inset of Fig. 1 for detwinned single crystals with $z = 0$ and 0.02 in which Zn does not affect the T-linear term in ρ_a. Particularly, in the case of the oxygen-reduced compound, even for the $z = 0.04$ where superconductivity disappears, the feature in $\rho_{ab}(T)$ around T^* remains, although the carriers tend to localize below 50 K. The results demonstrate that the Zn doping does not affect the characteristic temperature T^* in ρ_{ab} which indicates the temperature below which the spin gap starts to open.[2,3] Thus we may conclude that Zn doping increases the elastic scattering rate without much influencing the inelastic scattering process.

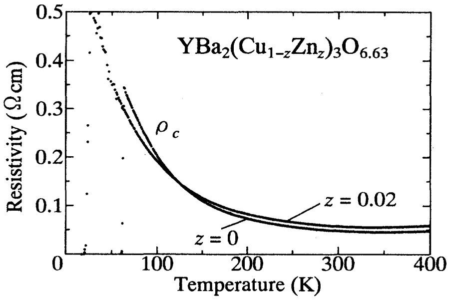

FIG. 2. Temperature dependence of the out-of-plane resistivity for the crystals with $z = 0$ and $z = 0.02$ ($y = 0.37$).

We show in Fig. 2 the temperature dependence of ρ_c for the oxygen-reduced crystals with and without Zn doping. The relationship between the interplane charge transport and the *spin gap* formation has recently been suggested for underdoped Y123.[4,8] It is shown that a crossover in $\rho_c(T)$ from metallic T dependence (at high temperatures) to nonmetallic one takes place at a temperature near T^*. In this regard, the semiconducting $\rho_c(T)$ is more sensitive to the opening of a gap or a pseudogap. It is remarkable that both magnitude and T dependence of ρ_c do not change with Zn doping, providing another evidence for the persistence of the spin gap in the Zn-doped compounds.

To get further insight into the effect of Zn doping on the in-plane charge transport, we measured Hall coefficient (R_H). Magnetic field is applied parallel to the c axis and the current flows in the ab plane. We show in Fig. 3 the temperature dependence of R_H for Zn-doped Y123 single crystals. For $y = 0.07$, R_H varies with T, being almost proportional to $1/T$. For the oxygen-reduced sample R_H deviates from the $1/T$ dependence below about 250 K and forms a peak at about 100 K. With increasing Zn concentration R_H increases over the entire temperature range,[20] but the temperature below which R_H starts to deviate from the $1/T$ behavior does not change [see the solid curves in Fig. 3

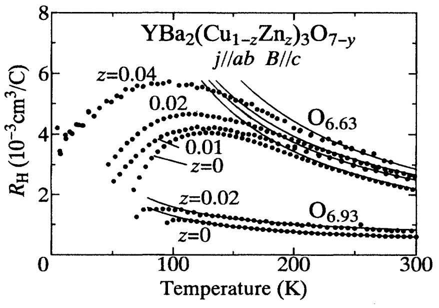

FIG. 3. Temperature dependence of the in-plane Hall coefficient for $YBa_2(Cu_{1-z}Zn_z)_3O_{7-y}$ with $y = 0.07$ and $y = 0.37$. The solid curves represent the $1/T$ fit to the data in the high-temperature region.

($R_H = A/T + B$) which best-fit the data in the high-temperature region]. Thus, the characteristic temperature in $R_H(T)$ which appears to coincide with T^* in ρ_{ab} dose not significantly change with Zn doping. We should note that the characteristic temperature in these transport coefficients does not change in sharp contrast to the rapid suppression of T_c. Therefore, it may be concluded that Zn does not affect the spectrum of excitations or a portion of their spectrum which couples with the charge dynamics in the normal state, even if it might seriously affect different parts of the spectrum which were responsible for superconducting pair formation.

Now we discuss the Zn-doping effect on the transport properties in relation with the magnetic properties investigated for Zn-doped Y123 and Y124. NMR studies have presented quite significant results of the Zn-doping effect on spin dynamics. For Y123 and Y124 which are in the underdoped regime, $(T_1T)^{-1}$ of Cu(2), proportional to the susceptibility $\chi''(Q,\omega\sim 0)$ with $Q=(\pi,\pi)$ representing antiferromagnetic (AF) wave vector shows a Curie-Weiss-like T dependence at high temperatures. As temperature goes down, $(T_1T)^{-1}$ is reduced relative to the Curie-Weiss behavior below a temperature indicating *spin gap* formation and as a result forms a peak well above T_c. Upon Zn doping the peak of $(T_1T)^{-1}$ is washed out and $(T_1T)^{-1}$ continues to increase with lowering temperature.[13] This result seems to indicate that the *spin gap* at $Q=(\pi,\pi)$ disappears, which was suggested also by the neutron inelastic scattering by Kakurai *et al.*,[21] showing that the spectral density in the low-energy region increases with Zn doping. On the other hand, the neutron experiment by Harashina *et al.*[22] have observed the spin gap feature at high temperatures while it almost disappears at low temperatures, possibley due to the disorder effect which creates a spin-glass-like state.

The sensitiveness of $(T_1T)^{-1}$ to Zn doping is in sharp contrast to the T dependences of $\rho_{ab}(T)$ and $\rho_c(T)$. In particular, $\rho_c(T)$, which is expected to have a more intimate connection with the spin gap,[4,8] shows no significant change with Zn doping. This fact may indicate that the spin gap at $q=Q$ has no direct connection to the charge transport.

In contrast to $(T_1T)^{-1}$, the Knight shift at Cu(2), ΔK, does not change appreciably with Zn doping, as demonstrated by the measurement on Zn-doped Y124 (Ref. 13) which is an intrinsically underdoped material. ΔK is proportional to the uniform susceptibility $\chi(q=0)$ and shows a sharp decrease with lowering T for any high-T_c cuprate in the underdoped regime. The NMR result indicates that the spin gap persists against Zn doping at least at $q=0$ and so that the spin gap is a local phenomenon,[23,24] that is, the development of the spin gap extends over most of the momentum space. As evidenced by the recent NMR experiment,[11] a Zn impurity affects the Cu(2) sites only in its vicinity and it does not change the global feature of the spin pseudogap. We may conclude that the charge transport has a connection with the global feature in the spin fluctuations in the momentum space, not with a particular spin gap, say, at $q=Q$.[25]

Figures 4(a) and 4(b) demonstrate how the in-plane resistivity mimics the uniform susceptibity. We plot in Fig. 4(a) $[\rho_{ab}(T)-\rho_{ab}(0)]/\alpha T$ vs T, where $\rho_{ab}(0)$ is the intercept of the T-linear part of $\rho_{ab}(T)$ at $T=0$ and α is the slope of the T-linear ρ_{ab}. For $\chi(0)$ we plot in Fig. 4(b) the static magnetic susceptibility $\chi_m(T)$ measured on the sintered pellets with the same Zn and oxygen contents and annealed in the same procedure.

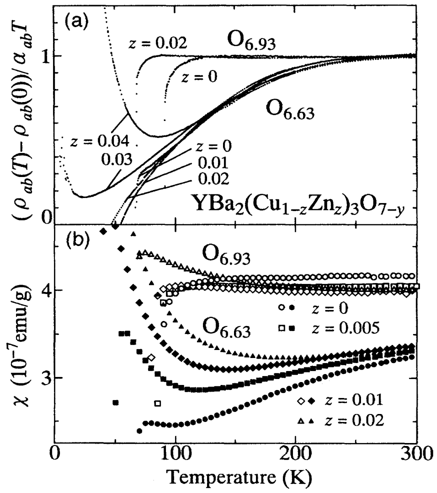

FIG. 4. (a) $[\rho_{ab}(T)-\rho_{ab}(0)]/\alpha_{ab}T$ as a function of temperature, where α_{ab} is the slope of the T-linear region of ρ_{ab} curve and $\rho_{ab}(0)$ is the extrapolated value to $T=0$ K from the T-linear region. (b) Temperature dependence of the magnetic susceptibility measured on the sintered pellets with the same oxygen contents as those of the single crystals utilized for resistivity measurement.

For the maximum oxygen content ($\sim$6.93) all the curves in Figs. 4(a) and 4(b) are nearly flat in the normal state, reflecting the T-linear ρ_{ab} and the Pauli-paramagnetic χ_m over a wide temperature range, respectively. The Zn doping does not cause any appreciable change in the T dependence of ρ_{ab}, and similarly the T dependence of χ_m remains nearly flat with a small Curie term seen for $z=0.02$, which corresponds to the magnetic moment of $\sim 0.2\mu_B$ or less per Zn.

The plots for the oxygen-reduced compounds are also similar in the high-temperature region, showing a characteristic decrease below $\sim$250 K. The effect of Zn doping does not change the main feature in the high-temperature region. A difference becomes apparent only in the low-temperature region, where a Curie term in χ_m due to local magnetic moments develops progressively with z. The induced moment is estimated to be $\sim 0.8\mu_B$ per Zn, consistent with the results of NMR and μSR experiments.[11,12] By contrast, an appreciable change is not seen in the resistivity data plotted in Fig. 4(a) for small Zn contents ($z<z_c$). A pronounced upturn, reminiscent of a Curie term in $\chi_m(T)$, appears only for nonsuperconducting $z=0.04$ reflecting a carrier localization at low temperatures.

A surprising fact is that the Curie term, an evidence for the localized magnetic moments induced by nonmagnetic Zn, manifests itself in $\chi_m(T)$ even for $z<0.04$, whereas the in-plane resistivity is metallic over the entire temperature range above T_c without showing any indication for carrier localization. This is quite anomalous in view of the NMR evidence that Cu($3d$) and O($2p$) holes forms a strongly hybridized state,[14] that is, the decoupling into localized Cu($3d$) spins and O($2p$) charge carriers does not take place in the CuO_2 plane. Formation of localized moments in the metallic state is a challenging problem for both Fermi liquid and non-Fermi liquid theories. In the Fermi liquid picture where the same electron carries both charge and spin, it seems hard to suppose that the strong impurities, in the unitarity scattering limit, produce localized magnetic moments in the metallic state. Actually, in the highly doped material, 90 K-Y123, Zn induces a reduced magnetic moment[11] and the magnetic moment is much more reduced in the overdoped $La_{2-x}Sr_xCuO_4$ with $x=0.30$.[26] Nagaosa and Ng have recently shown that a nonmagnetic impurity can induce localized moment when the spin gap is presumed in the uniform RVB state.[27]

In summary, we have investigated the Zn-doping effect on the transport properties of $YBa_2Cu_3O_{7-y}$ with particular emphasis on its underdoped spin gap phase. It is found that the doped Zn acts as a strong scatterer for the in-plane charge transport, but the principal feature in the T dependences of the transport coefficients, associated possibly with the opening of a spin pseudogap, is not affected by Zn doping. From these results we conclude that the charge transport has relevance to local spin fluctuations not restricted at $q=Q$ in the momentum space. It is also characteristic of the underdoped spin gap regime that Zn induces fairly large local magnetic moments ($\sim 0.8\mu_B$) even when charge carriers are not localized.

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[1] For a review, see N. P. Ong, in *Physical Properties of High-Temperature Superconductors II*, edited by D. M. Ginsberg (World Scientific, Singapore, 1990), p. 459.

[2] T. Ito, K. Takenaka, and S. Uchida, Phys. Rev. Lett. **70**, 3995 (1993).

[3] B. Bucher *et al.*, Phys. Rev. Lett. **70**, 3995 (1993).

[4] C. C. Homes *et al.*, Phys. Rev. Lett. **71**, 1645 (1993).

[5] H. Yasuoka, T. Imai, and T. Shimizu, in *Strong Correlation and Superconductivity*, edited by H. Fukuyama, S. Maekawa, and A. P. Malozemoff (Springer, Berlin, 1989), p. 254.

[6] J. Rossat-Mignod *et al.*, Physica (Amsterdam) **185-189C**, 86 (1991); P. M. Gehring *et al.*, Phys. Rev. B **44**, 2811 (1991).

[7] D. N. Basov *et al.*, Phys. Rev. B **50**, 3511 (1994).

[8] K. Takenaka *et al.*, Phys. Rev. B **50**, 6534 (1994).

[9] For example, B. Jayaram *et al.*, Phys. Rev. B **38**, 2903 (1988).

[10] H. Alloul *et al.*, Phys. Rev. Lett. **67**, 3140 (1991).

[11] A. V. Mahajan *et al.*, Phys. Rev. Lett. **72**, 3100 (1994).

[12] P. Mendels *et al.*, Phys. Rev. B **49**, 10 035 (1994).

[13] G. Zheng *et al.*, J. Phys. Soc. Jpn. **62**, 2591 (1993).

[14] H. Alloul, T. Ohno, and P. Mendels, Phys. Rev. Lett. **63**, 1700 (1989).

[15] H. C. Montgomery, J. Appl. Phys. **42**, 2971 (1971); B. F. Logan, S. O. Rice, and R. F. Wick, *ibid.* **42**, 2975 (1971).

[16] D. B. Haviland, Y. Liu, and A. M. Goldman, Phys. Rev. Lett. **62**, 2180 (1989).

[17] T. Wang *et al.*, Phys. Rev. B **43**, 8623 (1991).

[18] S. Tanda, M. Honma, and T. Nakayama, Phys. Rev. B **43**, 8725 (1991).

[19] T. R. Chien, Z. Z. Wang, and N. P. Ong, Phys. Rev. Lett. **67**, 2088 (1991).

[20] Although Zn doping increases the magnitude of R_H, this does not imply that the carrier density decreases with z. The Zn-doping dose not affect the carrier density as evidenced by the NMR study (Ref. 11) and also by the almost unchanged slope (α_{ab}) of the T-linear ρ_{ab} at high temperatures. Hence, R_H may be determined by a subtle balance between elastic and inelastic scattering of carriers.

[21] K. Kakurai *et al.*, Phys. Rev. B **48**, 3485 (1993).

[22] H. Harashina *et al.*, J. Phys. Soc. Jpn. **62**, 4009 (1993).

[23] P. Monthoux and D. Pines, Phys. Rev. B **49**, 4261 (1994).

[24] N. Nagaosa and P. A. Lee, Phys. Rev. Lett. **64**, 2450 (1990); Phys. Rev. B **45**, 966 (1992).

[25] Similar conclusion has been drawn from the recent thermopower measurement by J. R. Cooper *et al.* (unpublished), which indicates that Zn doping does not destroy the pseudogap but fills it in gradually.

[26] N. Ichikawa and S. Uchida (unpublished).

[27] N. Nagaosa and T-K. Ng (unpublished).