Increased phase-breaking scattering rate in Zn-doped $YBa_2Cu_3O_{7-\delta}$

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The in-plane resistance of two single crystals of $YBa_2(Cu_{1-0.01x}Zn_{0.01x})_3O_{7-\delta}$, $x=1$ and 3.5, was measured in magnetic fields up to 12 T parallel to the c axis at temperatures $\epsilon=\ln(T/T_c)$ up to about $\frac{1}{3}$. The coherence lengths and the phase-breaking scattering time τ_ϕ were determined. ξ_{ab} and ξ_c were both found to decrease with Zn doping, with a slow increase of the anisotropy ratio ξ_{ab}/ξ_c. The phase-breaking scattering rate $1/\tau_\phi$ increases strongly with increasing Zn concentration, indicating that Zn causes pair breaking in $YBa_2Cu_3O_{7-\delta}$.

The origin of the strong effect on the superconducting transition temperature, T_c, of doping Zn into $YBa_2Cu_3O_{7-\delta}$, is interesting and controversial. For $YBa_2(Cu_{1-0.01x}Zn_{0.01x})_3O_{7-\delta}$, depression rates in the range $-dT_c/dx=10\pm2$ K/% have been reported[1–8] with a few results of both smaller[9] and larger[10] values. The scatter of these results may be due to varying oxygen concentration, with a larger effect on T_c for oxygen deficient samples.[4] Nevertheless all data confirm a strong depression of T_c. For conventional superconductors magnetic pair breaking is the only known mechanism causing such a dramatic effect on T_c, and this picture has consequently often been suggested also for Zn in $YBa_2Cu_3O_{7-\delta}$. Other explanations include an influence on the hole carrier concentration in the planes,[11] or the possibility of *d*-wave pairing,[10,12] with a sensitivity to nonmagnetic impurities similar to magnetic impurities in conventional superconductors.

The starting point for the present work is the question if pair breaking can be verified or disproved from studies of superconducting fluctuations. If pair breaking is present, one would expect an increased phase-breaking scattering rate, τ_ϕ^{-1}, leading to reduced Maki-Thompson (MT) terms in the observed magnetoconductivity, $\Delta\sigma(T,B)$ $[=\sigma(T,B)-\sigma(T,0)]$.

This idea is hampered by difficulties in analyzing the experimental magnetoconductivity. First, in the temperature region where the fluctuations are large, the MT contributions are a minor part of the measured $\Delta\sigma(T,B)$, and at higher temperatures the small fluctuations and the strong temperature dependence of $\sigma(T,0)$ makes temperature regulation in magnetic field a major limit to experimental precision. Furthermore, in the clean limit of fluctuation theories, one can determine only the product $\tau_\phi\ell$ from the MT terms. ℓ is the electron mean free path. Therefore additional assumptions about ℓ must be made in order to extract τ_ϕ. Consequently the errors in τ_ϕ^{-1} determined from magnetoresistance are large.

In a recent study of fluctuations in the magnetoconductivity of Zn-doped $YBa_2Cu_3O_{7-\delta}$ it was concluded that Zn impurities do not act as magnetic pair breakers.[7] Unfortunately this analysis was limited to the small magnetic field of 1 T, and furthermore it is not clear what the accuracy of the fitting parameters obtained was.

In the present paper we report on measurements and analyses of $\Delta\sigma(T,B)$ in $YBa_2(Cu_{1-0.01x}Zn_{0.01x})_3O_{7-\delta}$ single crystals with $x=1$ and 3.5%. The measurements were extended up to temperatures $\epsilon=\ln(T/T_c)\approx\frac{1}{3}$ in magnetic fields to 12 T. More stringent fitting results are obtained from such an extended measurement range. The errors in τ_ϕ are nevertheless substantial. Different methods of analysis were therefore used. In all cases it was found that τ_ϕ decreases rapidly with Zn concentration.

Two samples of Zn-doped $YBa_2Cu_3O_{7-\delta}$ were prepared by a self-flux method as described previously.[13] Excess zinc oxide was carefully mixed with powders of copper and yttrium oxides and barium carbonate. Y_2O_3 stabilized ZrO_2 crucibles were used for crystal growing. Final oxygen annealing was performed at 450 °C for a few days. Zn concentration was determined from an analytical scanning electron microscope, by averaging over several samples from the same batch. The results of $x=1$ and 3.5% are believed to be accurate to within 10–20 %. Electrical contacts were made with silver paint and cured for 30 min at 450 °C in oxygen.

The midpoints of the resistive transitions and the widths of the transitions were 85.6 K (0.2 K) for 1% Zn and 70.0 K (1.5 K) for 3.5% Zn. The corresponding average depression rate of about 7 K/% is on the low side of the majority of data quoted above. The zero-field resistivity is shown in Fig. 1. Due to the small crystal size, the absolute values for the resistivities are uncertain. The approximately parallel curves suggest that Zn doping mainly affects the resistivity by increased elastic scattering. This is in agreement with previous investigations at comparable concentrations.[3,6,7]

Measurements were made with the current along the planes and the magnetic field $B\|c$ axis. The temperature was held constant and the magnetic field was swept from $0\rightarrow12\rightarrow0\rightarrow-12\rightarrow0$ T. A Pt thermometer located 20 cm above the sample where Helmholtz coils cancelled the magnetic field was used for temperature control. The temperature at the sample position in zero field was measured with an Ir thermometer. Temperature drift during one field sweep was typically below 40 mK. In most cases it was possible to compensate for this since the temperature drift was negligible during at least one half of the sweep.

The observed change of the conductivity in magnetic field, $\Delta\sigma(B,T)$ was analyzed by considering four contributions;

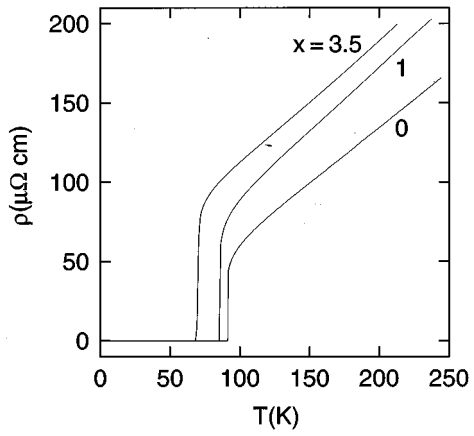

FIG. 1. The electrical resistivity of single crystals of $YBa_2(Cu_{1-0.01x}Zn_{0.01x})_3O_{7-\delta}$.

$$\Delta\sigma = \frac{1}{C}(\Delta\sigma_{\mathrm{ALO}} + \Delta\sigma_{\mathrm{MTO}} + \Delta\sigma_{\mathrm{ALZ}} + \Delta\sigma_{\mathrm{MTZ}}). \qquad (1)$$

AL means Azlamasov-Larkin, MT Maki-Thompson, O is an orbital contribution and Z a Zeeman term. C is a factor accounting for possible sample deficiencies. $C \geqslant 1$ unless the resistivity is underestimated. C can be estimated from the normal-state temperature derivative of the electrical resistivity.[14] A summary of these formulas, including references to the original work and some details of our fitting procedures are given in Ref. 15. Inclusion of a nonlocal effect has been suggested to be necessary;[16] however, adequate experimental support is still missing and this contribution has seldom been considered.

Some results and an analysis from Eq. (1) are shown in Fig. 2. For each sample three constants were determined; the coherence lengths ξ_{ab} and ξ_c, and τ_ϕ. The accuracy of these results was investigated by repeated analyses with different choices of C and the temperature dependence of τ_ϕ.

We first discuss the coherence lengths. The results for ξ_{ab} and ξ_c were found to be rather stable in different analyses and can be summarized as $\xi_{ab} = 14 \pm 1$ Å, $\xi_c = 2 \pm 0.5$ Å for 1.5% Zn, and $\xi_{ab} = 15 \pm 1$ Å, $\xi_c = 1.5 \pm 0.5$ Å for 3.5% Zn. The results were compared to those for a pure single crystal close to T_c, where data for $B \| c$ and $B \| ab$ were analyzed by the same procedures as presently employed.[15] The results are shown in Fig. 3

Contrary to our results, Semba and co-workers[7] found an increase in both coherence lengths and a reduction of anisotropy with increasing Zn concentration. We do not understand this difference but point out some observations supporting our results.

In the clean limit ξ decreases with reduced impurity mean free path ℓ_i as (Ref. 17) $\xi^{-1} = \xi_0^{-1} + \alpha \ell_i^{-1}$, where α is a constant of order 1 and ξ_0 the coherence length of ideal $YBa_2Cu_3O_{7-\delta}$ with an infinite mean free path. The curve for $\xi_{ab}(x)$ in Fig. 3 was calculated for $\alpha = 1$.[18] Considering the errors of the experimental results, this model qualitatively describes our results for $\xi_{ab}(x)$.

The anisotropy ratio $\gamma = \sqrt{m_c m_{ab}^{-1}}$ of Fe-doped $YBa_2Cu_3O_{7-\delta}$ has been obtained from studies of breaking of

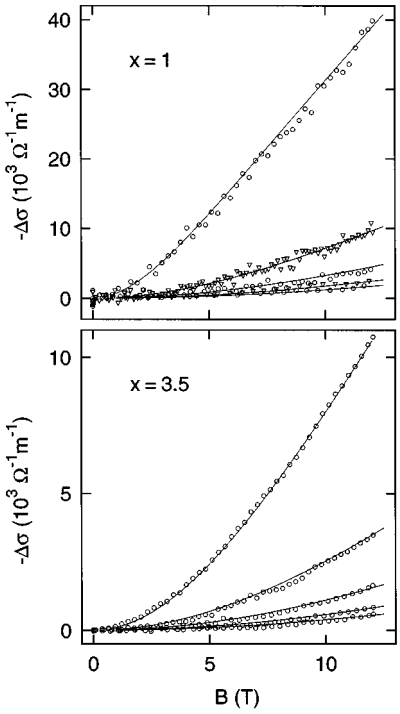

FIG. 2. Magnetoconductivity of Zn-doped samples. Top panel: 1% Zn. Temperatures are from top to bottom 90.0, 95.3, 100.2, 105.6, and 110.3 K. Bottom panel: 3.5% Zn. Temperatures are from top to bottom 75.9, 82.3, 89.5, 97.5, and 104.2 K. The curves are fits of Eq. (1).

vortices in the vortex liquid.[19] This method was recently applied to Zn-doped samples.[20] The results are shown in the lower panel of Fig. 3. The difference between γ values obtained from two widely different methods is not unreasonable, and the weak concentration dependence is similar. These observations give strong support to our analyses of $\Delta\sigma(B,T)$.

The clean limit of the theories was used to determine τ_ϕ. Good fits could also be obtained in the dirty limit, but these results for ξ_{ab} were not consistent with the requirement $\ell \ll \xi_{ab}$. Neglecting variations with Zn concentration of the carrier density (Ref. 21) n^* and effective mass m^* and assuming v_F to be constant, ℓ^{-1} was obtained from the measured ρ. For the pure sample we took (Ref. 15) $\tau_\phi = \tau_{\mathrm{tr}} = 35\ (100/T)$ fs with T in K. For $x > 0$, τ_ϕ was obtained from the fitted $\tau_\phi \ell$ by assuming two different temperature dependences of τ_ϕ; (i) τ_ϕ^{-1} proportional to T and (ii) τ_ϕ^{-1} proportional to $\tau_{\mathrm{tr}}^{-1}(x)$, i.e., of the form $a + bT$, where a/b was determined from the resistivity curves. Method (ii) thus contains the same number of fitting parameters as method (i), i.e., the two coherence lengths and the value of $\tau_\phi \ell$ at a chosen temperature taken to be 100 K. In addition, the analyses were repeated for a range of different values of C in Eq. (1), taking into account different unknown levels of imperfections in the crystals and to some extent errors in the resistivity measurements. When using results for $\tau_{\mathrm{tr}}^{-1}(x)$ evaluated from the values of $\rho(x)$ reported by Chien *et al.*,[3] it was found that τ_ϕ^{-1} increases even faster with Zn doping than the results obtained from our ρ values described below.

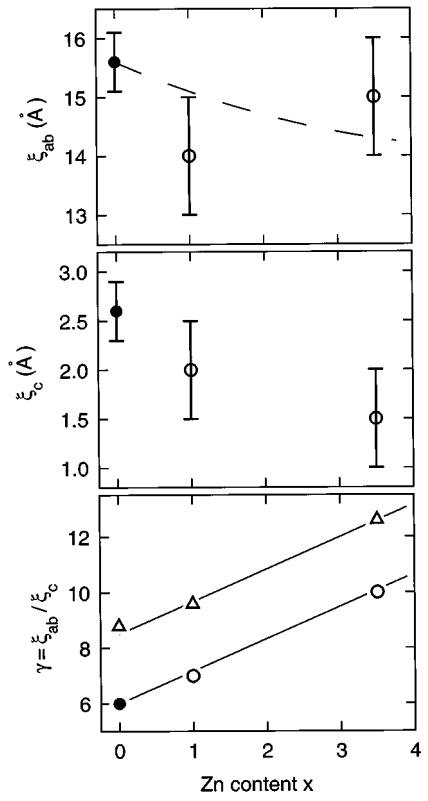

FIG. 3. ξ_{ab}, ξ_c, and the anistropy ratio $\gamma = \xi_{ab}/\xi_c$. ○: magnetoconductivity (present work); ○: magnetoconductivity (Ref. 15); △: vortex breaking (method of Ref. 19 and results from Ref. 20). The dashed curve for ξ_{ab} was calculated from the results for the magnetoresistance and a clean limit expression for the relation between the coherence length and the mean free path discussed in text.

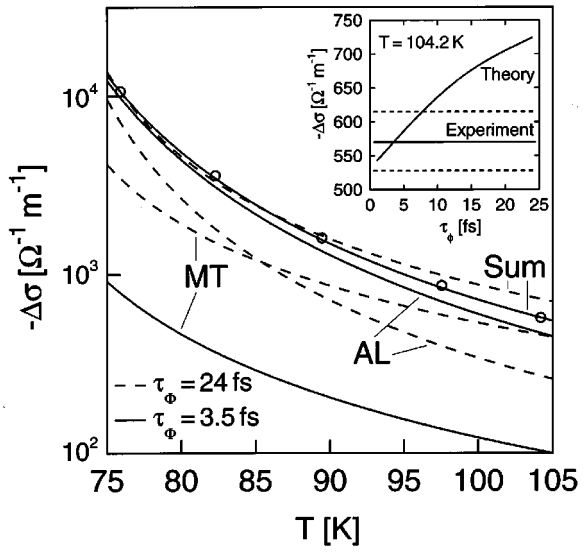

FIG. 4. Excess conductivity at 12 T vs temperature for the 3.5% Zn sample. The circles are observations. The full curves are MT and AL terms, and their sum $\Delta\sigma(T)$ obtained with $C=1.3$, $\xi_{ab}=15.3$ Å, $\xi_c=1.2$ Å, and $\tau_\phi=3.5$ fs. The dashed curves are the best fits when $\tau_\phi(100\text{ K})=\tau_{tr}(100\text{ K})=24$ fs ($C=1.3$, $\xi_{ab}=13.9$ Å, $\xi_c=3.5$ Å). Inset: calculated $\Delta\sigma$ at $T=104.2$ K and $B=12$ T vs τ_ϕ. The horizontal line is the observed value and the dashed lines are estimates of experimental errors. Although the actual value of τ_ϕ is uncertain it should be <8 fs.

In all calculations we have used $v_F=2.1\times10^5$ m/s.[7] A different choice would not affect the qualitative conclusions, but would change the scale of τ_ϕ.

τ_ϕ was found to decrease strongly with Zn concentration, x, in each of the analyses with different assumptions about $\tau_\phi(T)$ and varying choices of the C factor. A vanishing τ_ϕ implies large errors in the phase breaking scattering rate and the results for $d\tau_\phi^{-1}(x)/dx$ were found to fall in a wide range from about 0.2 to 2×10^{14} s^{-1} $(\%)^{-1}$. The several different analyses made provide confidence in the lower limit of the result: $\tau_\phi^{-1}(x)$ increases with Zn doping by at least 0.2×10^{14} $s^{-1}(\%)^{-1}$. This value is significantly larger than the increase of the transport relaxation rate; $d\tau_{tr}^{-1}(x)/dx\approx4\times10^{12}$ $s^{-1}(\%)^{-1}$ as estimated from the observed resistivity. Thus we can safely separate the concentration dependence of τ_ϕ from that in the parameter τ_ϕ used in the fitting procedures.

Our results are firmly based on observations and Eq. (1). Figure 4 shows the observed $\Delta\sigma(T)$ at 12 T for $x=3.5\%$ together with two sets of curves calculated from Eq. (1) with $C=1.3$ and $\tau_\phi(T)$ as in method (i) above. The full curves are AL and MT components and their sum for $\tau_\phi=3.5$ fs. An excellent description of the data can be obtained. For the dashed curves it was assumed that $\tau_\phi(100\text{ K})=\tau_{tr}(100\text{ K})=24$ fs and the best fits were calculated with the coherence lengths as freely varying parameters. The MT terms are now larger by a factor of 5 and for $T>90$ K the best $\Delta\sigma(T)$ is significantly larger than observations. The value of τ_ϕ at $x=3.5\%$ is quite uncertain but it must be small. The inset shows $\Delta\sigma$ calculated at $B=12$ T and $T=104.2$ K for a range of values of τ_ϕ. At each τ_ϕ, ξ_{ab} and ξ_c were adjusted. If $\tau_\phi>8$ fs, the calculated $\Delta\sigma$ is inconsistent with observations within estimated errors. The resulting anisotropy ratio γ decreases with increasing τ_ϕ and is <7 for $\tau_\phi>8$ fs. Such a result would thus also violate the trend in Fig. 3, which includes independent information that γ should increase with x.

Strong phase-breaking scattering by Zn impurities could be associated with magnetic pair breaking, which in this case presumably would occur through polarization of the Cu ions in the planes.[22] One cannot simply identify τ_ϕ^{-1} with the pair-breaking rate in the Abrikosov-Gorkov (AG) theory,[23] since the resulting depression, $T_c(0)-T_c(x)=\hbar\pi\tau_\phi^{-1}(x)/4k_B$, would then be 10–100 times larger than the observed rate and the observed resistivity increase is smaller than the increase of the phase-breaking rate. With a temperature-dependent pair breaking as in the Müller-Hartmann theory, the depression of T_c can become much smaller than in the AG theory for certain ranges of the ratio of T_c and the Kondo temperature.[24] The stronger increase of $\tau_\phi^{-1}(x)$ than of $\tau_{tr}^{-1}(x)$ is unconventional, and suggests that pair breaking is not necessarily observable in the normal-state resistivity. A similar conclusion that Zn doping affects different aspects of charge dynamics in the normal and superconducting states was recently made from Hall effect studies.[25] Furthermore, phase-breaking scattering of nonmagnetic origin cannot be

ruled out. Since the nature of the pairing state is not known, it is not certain that magnetic scattering is pair breaking.

Summarizing, we have demonstrated by a number of different analyses of the magnetoconductivity that τ_ϕ in Zn-doped $YBa_2Cu_3O_{7-\delta}$ decreases strongly with Zn concentration. Consistent results for τ_ϕ, ξ_c, ξ_{ab}, and the anisotropy provide confidence in these analyses. Thus Zn causes pair breaking in $YBa_2Cu_3O_{7-\delta}$. At present we cannot ascertain the nature of this pair breaking.

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