Impurity effects on the superconducting coherence length in Zn- or Ni-doped $YBa_2Cu_3O_{6.9}$ single crystals

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The superconducting coherence length ξ of Zn- or Ni-doped $YBa_2Cu_3O_{6.9}$ single crystals was measured through the diamagnetic susceptibility in the reversible region, and through the resistivity in the mixed state. Upon impurity doping, ξ increases along both the in- and out-of-plane directions, which suggests that the doped impurities act as pair breakers. The in-plane ξ is well explained by the pair-breaking theory of *d*-wave superconductivity. On the other hand, the increase of the out-of-plane ξ is larger than the theoretical prediction, which might indicate that the interplane coupling of the order parameter is modified by the impurities. [S0163-1829(99)06625-4]

Impurity effects in high-T_c cuprates (HTSC's) have long been a subject of intense debate.[1] In the beginning, that nonmagnetic Zn^{2+} suppresses the superconducting transition temperature T_c as much as (or even more effectively than) magnetic Ni^{2+} was a mystery. Considering that increasing evidence of the *d*-wave superconductivity in HTSC's, we can now understand it in terms of the pair-breaking effect in anisotropic superconductivity. However, there is still no consensus on how the impurity breaks the superconducting pair. According to Sun and Maki,[2] a standard treatment of impurity scattering (as Abrikosov and Gor'kov did in *s*-wave superconductivity) well explains the T_c reduction, on the assumption that the order parameter is suppressed uniformly in space by impurities. On the other hand, Uemura[3] has proposed that the order parameter becomes spatially inhomogeneous by impurity doping, and its amplitude is fully suppressed near the impurities.

To address this issue, it will be crucial how the superconducting coherence length ξ changes with impurities. In particular, since the in-plane superconductivity of HTSC is in the clean limit,[4] the in-plane coherence length ξ_{ab} is written as $\xi_{ab} \sim \hbar v_F^{ab}/\Delta$, where v_F^{ab} and Δ are the in-plane Fermi velocity and the (maximum) superconducting gap. Accordingly ξ_{ab} can be a measure of Δ. Semba, Matsuda and Ishii[5] have evaluated the Zn-doping effects on ξ of $YBa_2Cu_3O_{6.9}$ crystals by fitting the mixed-state resistivity with the superconducting fluctuation theory.[6] With the same technique, Watanabe and Matsuda[7] have studied the Co-doped $Bi_2Sr_2CaCu_2O_8$. In these works, ξ is obtained through complicated fitting, and it is desirable to obtain ξ in a simpler way.

Here we report on the measurements and analyses of the anisotropic coherence lengths of Zn- or Ni-doped $YBa_2Cu_3O_{6.9}$ (YBCO) crystals prepared by a crystal-pulling technique. The coherence lengths are evaluated through both the diamagnetic susceptibility and the mixed-state resistivity. Susceptibility is more advantageous than resistivity, because (i) it is a thermodynamic quantity reflecting the bulk nature, (ii) the transition temperature $T_c(H)$ is well defined, and (iii) no fitting is necessary to obtain ξ through $T_c(H)$.[8] A large size of our crystals enables us to measure it precisely in all directions. The measured ξ is increased with impurities along both the in- and out-of-plane directions. While the increase of ξ_{ab} is quantitatively explained by the theory of Sun and Maki,[2] the out-of-plane coherence length ξ_c exhibits an anomalously large increase beyond the theoretical prediction.

We prepared single crystals of $YBa_2(Cu_{1-x}M_x)_3O_y$ with $x=0.004$, 0.006 for Zn, $x=0.010$ for Ni, and $x=0$ (pure YBCO) by the solute rich liquid crystal pulling (SRLCP) method.[9] After initial growth of pure YBCO on MgO single crystal, an appropriate amount of substituents, 99.99% grade ZnO or NiO, was charged to the SRLCP molten. The grown crystals' compositions were analyzed by the inductively coupled plasma (ICP) analysis. Within the detection limit of ICP analysis, no undesirable impurity was detected. Each crystal (typical size of 10×10 mm^2 in the ab plane and 5 mm in the c axis) was cut into a rectangular shape and annealed in flowing O_2 for 200 h at 500 °C, and terminated with rapid quench to room temperature. Thus obtained samples are optimally doped with twinned structure. By Zn or Ni doping, T_c of 93 K for pure YBCO is suppressed down to 85 K for Zn=0.4%, 82 K for Zn=0.6%, and 87 K for Ni=1.0%. These T_c reductions are consistent with the literature,[1] and warrant the uniform substitutions in these crystals. Sharp transitions ($\Delta T_c \sim 1$ K) also support the crystal qualities.

The magnetization of the samples were measured by a commercial superconducting quantum interference device magnetometer (QD-MPMS-XL7), and magnetic field H was applied for $H \parallel c$ and $H \perp c$ configurations up to 7 T. In-plane

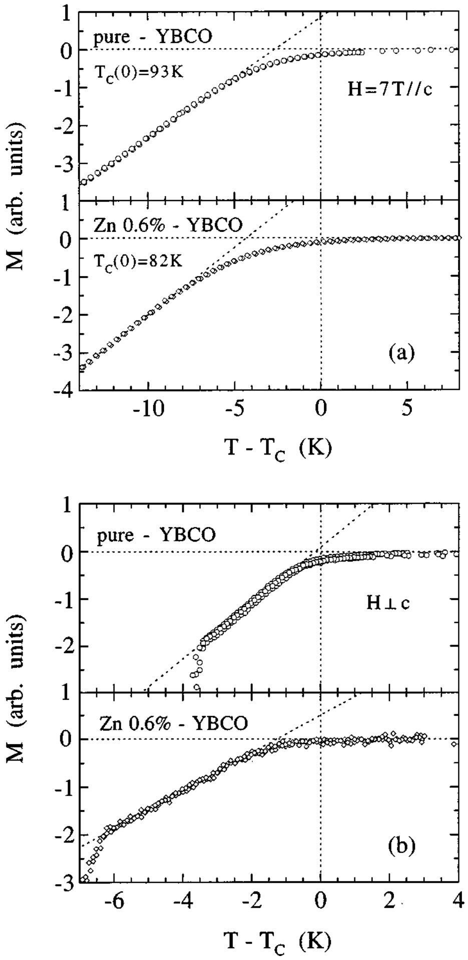

FIG. 1. Temperature dependence of the magnetization for pure $YBa_2Cu_3O_{6.9}$ (upper panel) and Zn=0.6% doped $YBa_2Cu_3O_{6.9}$ (lower panel) in a magnetic field H of 7 T. (a) H parallel to the c axis and (b) H perpendicular to the c axis.

resistivity ρ_{ab} was measured by a standard four-terminal method. Typical sampling current density was around 5 A/cm^2, and H was applied parallel to the c axis of the samples. All the resistivity measurements were done in the field-cooling condition.

Typical magnetizations in 7 T are shown in Fig. 1(a) for $H \| c$, and in Fig. 1(b) for $H \perp c$. Note that the data are taken in both cooling from T_c and warming to T_c, to specify the temperature range for the reversible magnetization. The upper panels are the results of pure YBCO and the lower ones for Zn=0.6% doped YBCO. The critical temperature in magnetic field $T_c(H)$ is evaluated from the cross point of the linear slope of the reversible magnetization curve below T_c and the normal state basal line.[8] Reflecting the two-dimensional nature, the two samples show a larger $T_c(0) - T_c(H)$ for $H \| c$ than for $H \perp c$. Since ξ is proportional to $|dH_{c2}/dT|$, this indicates that ξ_c is shorter than ξ_{ab}. It should be noted that $T_c(0)$-$T_c(H)$ is larger in Zn doped YBCO than in pure YBCO, which means that Zn doping increases ξ.

In Fig. 2, we plotted $T_c(H)$ for all the samples in the H-T diagram, from which $H_{c2}(T)$ can be evaluated. Considering that $H_{c2}(T)$ for each sample is roughly linear in T, we can apply the Werthamer-Helfand-Hohenberg formula given as[10]

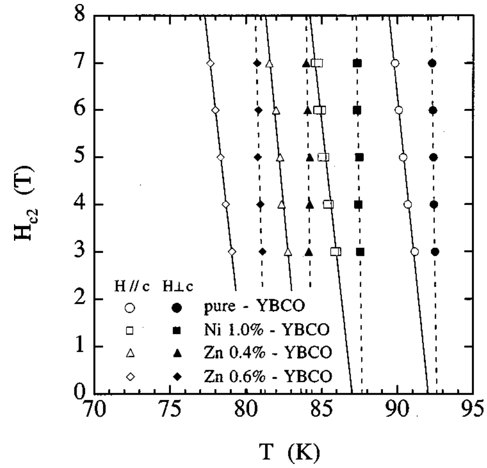

FIG. 2. Temperature dependence of the upper critical field of all the samples. The open (closed) symbols represent the magnetic field parallel (perpendicular) to the c axis.

$$H_{c2}(0) = 0.7 \left. \frac{\partial H_{c2}(T)}{\partial T} \right|_{T=T_c} T_c .$$

Then, ξ is evaluated through the relations of $H_{c2}(0) = \phi_0/2\pi\xi_{ab}^2$ for $H \| c$, and $H_{c2}(0) = \phi_0/2\pi\xi_{ab}\xi_c$ for $H \perp c$, where ϕ_0 is the quantum fluxoid $(=hc/2e)$. In Fig. 3(a), the thus obtained ξ_{ab} and ξ_c are plotted as a function of $1-(T_c/T_{c0})$, where T_{c0} represents T_c for pure YBCO. As clearly shown in Fig. 3(a), impurity substitution increases both ξ_{ab} and ξ_c. This implies that the impurity weakens the superconductivity to decrease Δ. Quantitatively, however, the amount of increase in ξ_c is not understandable; it is by twice for Zn=0.6% doping, while T_c is reduced only by 10%. A similar increase of ξ_c was already reported in Ref. 5.

Now let us discuss the increase of ξ_{ab}. As mentioned above, $1/\xi_{ab}$ is proportional to Δ in the clean limit. Although the doped Zn or Ni acts as a strong scatterer to shorten the mean free path (l) of carriers, the evaluated l is about 50-100 Å just above T_c for Zn=0.6% doped YBCO,[5] which still satisfies a condition of the clean limit ($\xi \ll l$). We would like

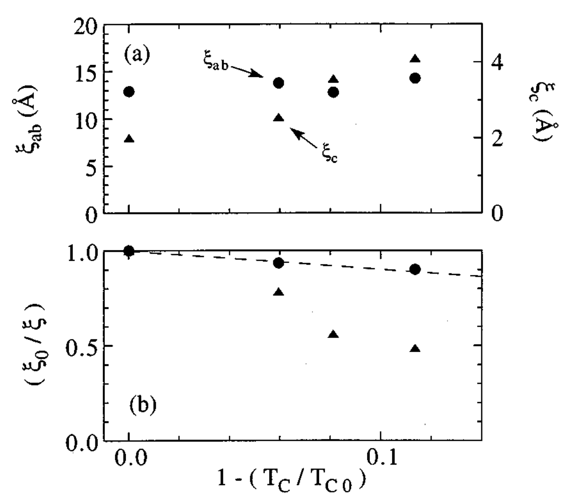

FIG. 3. (a) ξ and (b) (ξ_0/ξ) plotted as a function of 1-(T_c/T_{c0}), where T_{c0} and ξ_0 represent T_c and ξ for pure $YBa_2Cu_3O_{6.9}$. The dashed line is the theoretical calculation by Sun and Maki (Ref. 2).

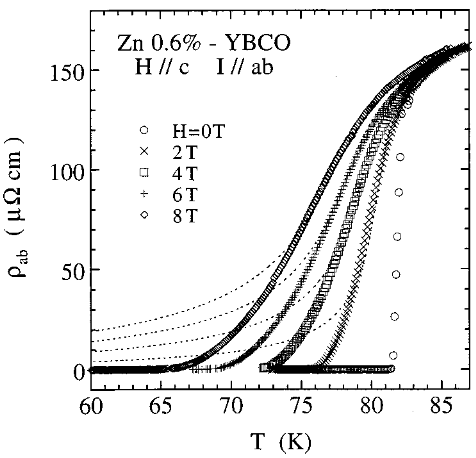

FIG. 4. The in-plane resistivity of the Zn = 0.6% doped $YBa_2Cu_3O_{6.9}$ crystal in magnetic field parallel to the c axis. The dotted curves are calculated from fluctuation theory (Ref. 6). The parameters used for fitting are as follows. The in-plane coherence length $\xi_{ab} = 12$ Å, the out-of-plane coherence length $\xi_c = 3$ Å, the critical temperature $T_c = 82$ K, the specific-heat jump $\Delta C = 47.2$ mJ/cm^{3}K, the conversion factor $C = 1.9$, and the conduction layer spacing $s = 11.7$ Å.

to emphasize that Zn or Ni doping does not change v_F^{ab} or the carrier density.[1] Hence the relative change of $1/\xi_{ab}$ with impurities is reduced to the relative change of Δ. We plot ξ_0/ξ in Fig. 3(b), where ξ_0 is ξ for pure YBCO. Note that ξ_{ab0}/ξ_{ab} is in excellent agreement with the theoretical calculation of Δ/Δ_0 shown by the dashed line (Δ_0 is Δ for pure YBCO).[2] We thus conclude that the suppression of the order parameter by impurities is quantitatively understood by Ref. 2.

The successful explanation by Ref. 2 seems to disagree with the strong suppression of the superconducting pair density by Zn doping, as observed in μSR (Ref. 3) or infrared conductivity.[11] We claim that these experiments do not contradict themselves; they are done in different parts of the H-T diagram. Since the present study is the measurement near H_{c2}, the order parameter is small enough to be homogeneous in space, which justifies the treatment of ''averaging'' the impurity scattering. At low temperatures (and $H \ll H_{c2}$) where the amplitude of the order parameter fully grows, we have to consider two cases depending on the coherence volume $\xi_{ab}^2\xi_c$. When $\xi_{ab}^2\xi_c$ is small enough to pay negligible cost to break the superconductivity locally, the superconductivity is likely to be suppressed near impurities. On the contrary, when $\xi_{ab}^2\xi_c$ is large, the order parameter favors to be uniform. Perhaps HTSC's are the former case, and superconductivity is robust in spite of a large amount of unpaired carriers induced by impurities.[11] We therefore propose that the coherence volume determines how to suppress the superconductivity at $T = 0$, which should be further clarified both experimentally and theoretically.

To verify the rapid increase of ξ_c by impurities, we measured the mixed-state resistivity. Figure 4 shows the temperature dependence of ρ_{ab} for $H \| c$ for the Zn = 0.6% doped YBCO. Using the superconducting fluctuation theory,[6] we successfully fit the resistive transition, as the dotted curves in Fig. 4. Because of the pinning effect, the lower resistivity

TABLE I. The transition temperatures (T_c) and the coherence lengths (ξ_{ab} and ξ_c) of all the samples. Note that the coherence lengths are obtained from both magnetization and resistivity measurements.

		Magnetization		Resistivity	
Sample	T_c (K)	ξ_{ab} (Å)	ξ_c (Å)	ξ_{ab} (Å)	ξ_c (Å)
pure	93	12.9	2.00	10.0	1.70
Ni 1.0 %	87	13.8	2.55		
Zn 0.4 %	85	12.8	3.56	10.4	1.90
Zn 0.6 %	82	14.3	4.10	10.5	2.00

curves at lower temperatures are out of the applicable region of the theory. The coherence lengths estimated by fitting ρ_{ab} qualitatively agree with the susceptibility measurement, as listed in Table I. We note that ξ obtained from the resistivity is well consistent with Ref. 5.

In conventional superconductors including superconducting multilayers, all the anisotropic properties are attributed to the anisotropic effective mass.[12] So far YBCO has been believed to be the case, because it is the least anisotropic HTSC.[13] In this case the coherence-length ratio ξ_{ab}/ξ_c would be independent of impurities. The measured ξ_{ab}/ξ_c is, however, strongly dependent on impurities, as shown in Fig. 5. An alternative approach is to introduce an interplane coupling such as the Josephson junction. As we have pointed out in our previous papers, the electronic states and charge dynamics of YBCO are essentially two dimensional, and their anisotropy cannot be ascribed only to the effective mass.[14] The anomaly in ξ_c might be another piece of the evidence. In this scenario, the increase of ξ_c suggests that the interplane coupling is increased upon impurity doping. Panagopoulos *et al.*[15] have found that the penetration depth becomes more isotropic with Zn doping, which they ascribed to the enhancement of the interplane coupling by Zn doping.

In summary, we have successfully grown the Zn- or Ni-doped $YBa_2Cu_3O_{6.9}$ single crystals by the crystal pulling method and examined the impurity effects on the coherence length and its anisotropy ratio. The observed impurity dependence of the in-plane coherence length is in an excellent agreement with the prediction of the pair-breaking theory in the d-wave superconductivity. However, the rapid increase in the out-of-plane coherence length cannot be explained by the

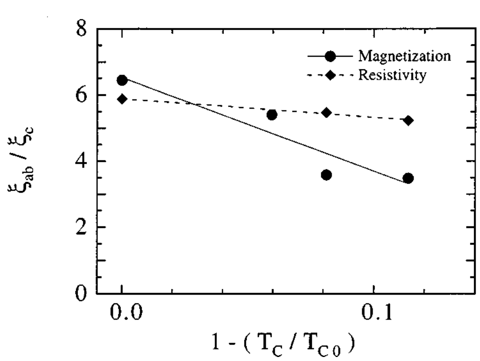

FIG. 5. The anisotropic ratio of the coherence length ξ_{ab}/ξ_c plotted as a function of 1-(T_c/T_{c0}).

conventional pair-breaking picture, which might correspond to the nature of the coupling mechanism of the superconducting layers in high-T_c superconductors.

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