Effects of Zn doping on the anisotropic penetration depth of $YBa_2Cu_3O_7$

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We have investigated the temperature (T) and doping dependences of the anisotropic magnetic penetration depth λ of high-quality grain-aligned $YBa_2(Cu_{1-x}Zn_x)_3O_7$ with $x=0.00$, 0.02, 0.03, and 0.05 using the ac-susceptibility technique. The values of the in-plane, $\lambda_{ab}(0)$, and out-of-plane, $\lambda_c(0)$, penetration depths were found to increase strongly with increased Zn concentration whereas the anisotropy ratio $\gamma=[\lambda_c(0)/\lambda_{ab}(0)]$ decreased. With increased Zn doping the $[\lambda_{ab}(0)/\lambda_{ab}(T)]^2$ and $[\lambda_c(0)/\lambda_c(T)]^2$ curves systematically approach each other. [S0163-1829(96)51642-5]

In $YBa_2Cu_3O_7$ (YBCO), one of the substituents of much interest is Zn, with a nonmagnetic d^{10} configuration, because it replaces the in-plane copper atoms Cu(2) and rapidly suppresses the superconducting transition temperature T_c.[1] Previous penetration depth studies[2] showed that as little as 0.31% Zn substitution causes a crossover from a linear temperature T dependence of the in-plane penetration depth to a T^2. This was interpreted as the effect of strong scattering on a d-wave superconductor.[3] The reason Zn causes a rapid decrease in T_c is still unclear. On the basis of the existence of a linear term in the heat capacity data below T_c it was initially suggested that Zn acts as a pair breaker.[4] Since then, others have proposed that Zn induces a small magnetic moment on neighboring Cu sites[5,6] and that magnetic scattering is responsible for the depression of T_c. On the other hand, recent analysis[7] of specific heat and susceptibility data of Zn-doped YBCO and $La_{2-x}Sr_xCuO_{4-y}$ leads to a picture in which Zn doping simply causes a shift of spectral weight to low energies rather than the formation of a true magnetic moment on neighboring Cu sites. The latter picture is perhaps more consistent with the NMR study of Ishida *et al.*[8] where well-defined magnetic moments on Ni atoms, which also substitute on the Cu(2) sites of YBCO, have a much smaller effect on the low-temperature Knight shift than Zn.

To the best of our knowledge, there are no systematic studies on the effects on Zn doping to the absolute values and T dependences of the in-plane, λ_{ab}, and out-of-plane, λ_c, magnetic penetration depths of the cuprates. Furthermore, no concrete theory is currently available to predict the possible effects of high concentrations of scattering impurities to the anisotropic penetration depth of d-wave superconductors. It is thus important to have systematic experimental evidence to determine the empirical effects of Zn substitution. Here we report the absolute values and T dependences of λ_{ab} and λ_c for high-quality magnetically aligned YBCO, which show large systematic changes with Zn content.

$YBa_2(Cu_{1-x}Zn_x)_3O_7$ samples with $x=0.00$, 0.02, 0.03, and 0.05 were prepared by solid state reaction, from CuO, Y_2O_3, ZnO, and $BaCO_3$. Each sample was lightly ground and sedimented in acetone to obtain well-defined grain size distributions. The sedimented powders were heat treated to repair any structural damages to the surface of the grains.[9] After the heat treatment, part of the collected powder for each Zn concentration was used to determine the grain-size distribution by analyzing scanning electron microscopy photographs. The average grain diameter for all samples studied here was 5 μm (50% cumulative volume point). The powders were mixed with a 5 min fast curing epoxy and aligned in a static field of 12 T at room temperature. From analysis of the x-ray rocking curves more than 90% of the sample was found to be c-axis aligned to within $\pm 1.4°$. The T_c's for the three different Zn compositions were 92.5 K, 68.2 K, 55 K, and 46.4 K for $x=0.00$, 0.02, 0.03, and 0.05, respectively, in reasonable agreement with values reported previously in the literature for fully oxygenated samples of similar Zn contents.[6] Actually our unpublished data for several sets of Zn:YBCO samples show that the T_c value of the 0.05 Zn sample corresponded to 0.045 Zn. We use the latter value in subsequent analysis. Hereafter T_c represents the temperature where the onset of superconductivity occurs in the ac susceptibility data for a measuring field $H_{ac}=3$ G rms and frequency $f=333$ Hz. ac susceptibility (χ) measurements were performed with the ac field applied either in the ab plane or along the c axis. Details of the experimental technique can be found in earlier publications.[10,11] The χ data were analyzed on the basis of the model first suggested by Shoenberg,[12] and the variation of λ with temperature for both orientations was obtained.[10,11]

The values of T_c, $\lambda_{ab}(0)$, $\lambda_c(0)$, and the anisotropy ratio

TABLE I. Table of T_c, $\lambda_{ab}(0)$, $\lambda_c(0)$, and $[\lambda_c(0)/\lambda_{ab}(0)]$ as a function of $x=0.00$, 0.02, 0.03, and 0.05 for $YBa_2(Cu_{1-x}Zn_x)_3O_7$.

x	T_c (K)	$\lambda_{ab}(0)$ (μm)	$\lambda_c(0)$ (μm)	$\lambda_c(0)/\lambda_{ab}(0)$
0.00	92.5	0.14	1.26	9.0
0.02	68.2	0.26	1.42	5.6
0.03	55.0	0.30	1.55	5.2
0.05	46.4	0.37	1.64	4.4

$\gamma=[\lambda_c(0)/\lambda_{ab}(0)]$, for the Zn concentrations studied here are listed in Table I. As T_c is reduced by Zn doping, $\lambda_{ab}{}^{-2}(0)$ falls very quickly. The fall is even faster than the Uemura relation[13] $\lambda_{ab}{}^{-2}(0)\propto T_c$ (not shown), which holds for underdoped materials where T_c is reduced by lowering the carrier concentration rather than by adding impurities to the CuO_2 planes. Our $\lambda_{ab}(0)$ values for $x\geq 0.02$ are in good agreement with those obtained from muon spin relaxation measurements on optimally doped polycrystalline $Y_{0.8}Ca_{0.2}Ba_2(Cu_{1-y}Zn_y)_3O_{y-\delta}$.[14] In the latter work the Cu-O chain contribution to $\lambda_{ab}(0)$ was deliberately suppressed by incorporating Ca and adjusting the oxygen content for maximum T_c. This implies that in our work the Cu-O chain contribution has been suppressed by $x=0.02$ or more Zn which is consistent with the analysis described later.

The temperature dependences of λ_{ab} and λ_c are shown in Figs. 1(a) and 1(b) as plots of $1/\lambda^2$ versus T because in the London model $1/\lambda^2=4\pi n_s e^2/m^*$, where n_s is the superfluid density and m^* is the effective mass. Figure 1(a) shows that as Zn is added the quasilinear dependence of $1/\lambda_{ab}{}^2(T)$ gradually evolves into a T^2 behavior at low T consistent with the single crystal results at lower x values.[2] On these unnormalized plots the slopes near T_c are independent of x for $x\geq 0.02$. Figure 1(b) shows that $1/\lambda_c{}^2(T)$ for $x=0.00$ also has an initial linear dependence at low T but is much flatter. The low-temperature data of λ_c is the first evidence for a clear linear T dependence of the out-of-plane penetration depth in YBCO. Possible explanations for this behavior are given below. This linear dependence becomes T^2 with the addition of Zn. Again the slopes near T_c are independent of x for $x\geq 0.02$. Normalized plots of $[\lambda(0)/\lambda(T)]^2$ versus T/T_c are shown in Figs. 2(a) and 2(b). These show similar overall behavior for $\lambda_{ab}(T)$ in the region $0<x\leq 0.03$ and for $\lambda_c(T)$ for $0.02<x\leq 0.05$.

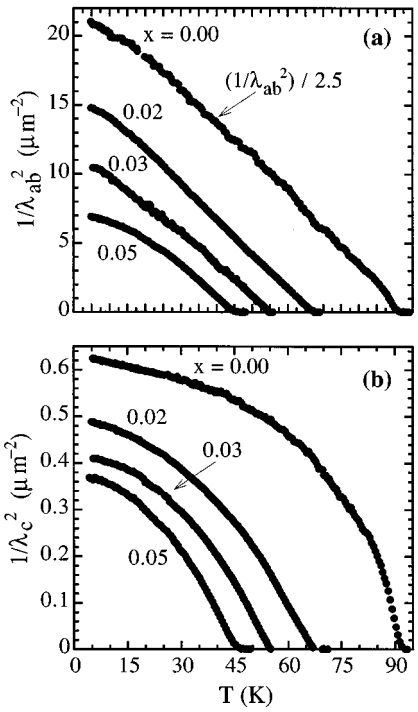

FIG. 1. Plots of (a) $(1/\lambda_{ab})^2$ and (b) $(1/\lambda_c)^2$ as functions of T for $YBa_2(Cu_{1-x}Zn_x)_3O_7$ with $x=0.00$, 0.02, 0.03, and 0.05. The $[1/\lambda_{ab}{}^2(T)]$ data for $x=0.00$ in (a) have been divided by 2.5 for clarity.

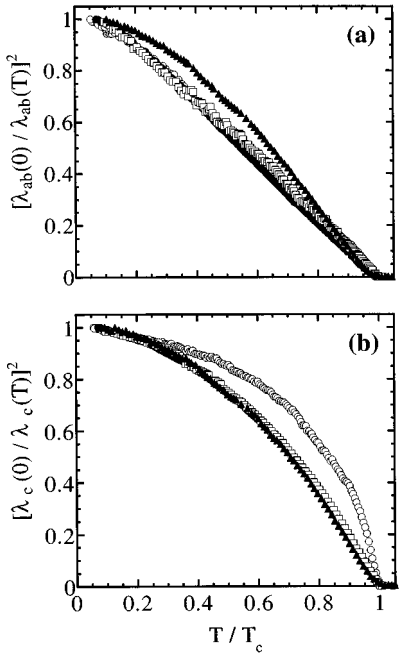

FIG. 2. Plots of (a) $[\lambda_{ab}(0)/\lambda_{ab}(T)]^2$ and (b) $[\lambda_c(0)/\lambda_c(T)]^2$ as functions of T/T_c for $YBa_2(Cu_{1-x}Zn_x)_3O_7$ with $x=0.00$ (open circles), 0.02 (closed circles), 0.03 (open squares), and 0.05 (closed triangles).

Figure 3(a) shows a comparison of $\lambda_{ab}(T)$ with $\lambda_c(T)$, plotted as $[\lambda_{ab}(0)/\lambda_{ab}(T)]^2$ and $[\lambda_c(0)/\lambda_c(T)]^2$, for $x=0.00$ and also the behavior expected for a weak coupling BCS d-wave superconductor.[15] There is striking agreement between $\lambda_{ab}(T)$ and the d-wave curve over the whole temperature range, which is in agreement with previous results for $HgBa_2Ca_2Cu_3O_{8+\delta}$ (Hg-1223).[11] As mentioned earlier in the text, although $[\lambda_c(0)/\lambda_c(T)]^2$ is flatter it is linear below 30 K [see inset to Fig. 3(a)]. In Hg-1223[11] which is much more anisotropic, $\lambda_c(T)$ was even flatter and this was ascribed to Josephson coupling between the planes. In the present case the anisotropy is much smaller and other possibilities for example proximity effect coupling via the Cu-O chains[16] or a variation in the c-axis transfer integral around the CuO_2 plane Fermi surface[17] should be analyzed further.

Figure 3(b) shows that for $x=0.05$, $[\lambda_{ab}(0)/\lambda_{ab}(T)]^2$ and $[\lambda_c(0)/\lambda_c(T)]^2$ have essentially the same T dependence. (The data are also compared with the behavior ex-

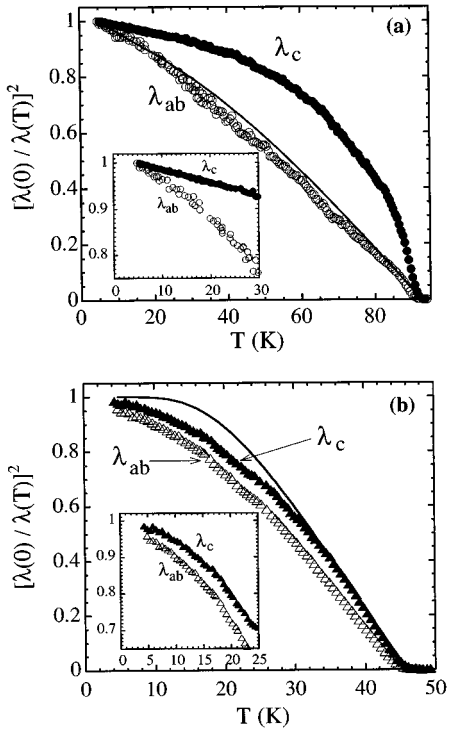

FIG. 3. Plots of $[\lambda_{ab}(0)/\lambda_{ab}(T)]^2$ and $[\lambda_c(0)/\lambda_c(T)]^2$ as functions of T for $YBa_2(Cu_{1-x}Zn_x)_3O_7$ with $x=0.00$ (a) and $x=0.05$ (b). Also shown, by the solid lines, in (a) is the theoretical prediction for the normalized superfluid density from the weak coupling BCS theory for a d-wave superconductor[15] and in (b) the weak coupling BCS theory for an s-wave superconductor.[18] The insets show the low-temperature regions.

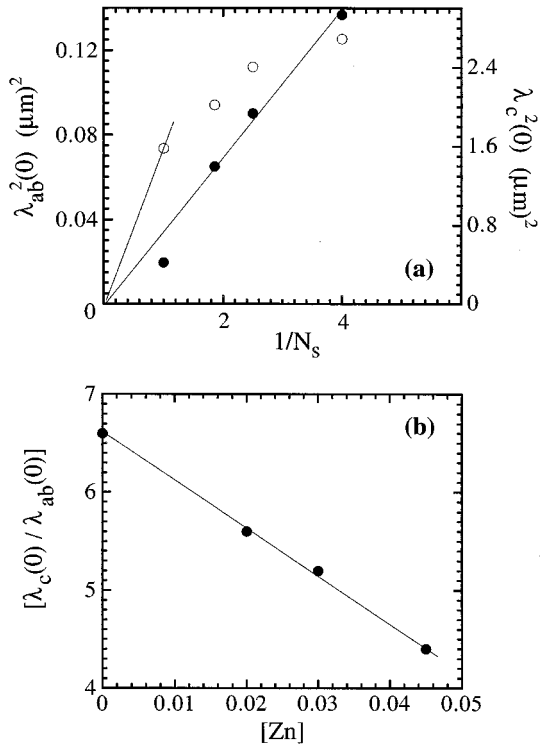

FIG. 4. (a) $\lambda_{ab}{}^2(0)$ (closed circles) and $\lambda_c{}^2(0)$ (open circles) versus $1/N_s$ for $YBa_2(Cu_{1-x}Zn_x)_3O_7$ with $x=0.00$, 0.02, 0.03, and 0.05. Here $N_s=N_T-N_R$, where N_T is the total density of states and N_R the residual density of states below T_c which corresponds to unpaired electrons.[19] (b) $[\lambda_c(0)/\lambda_{ab}(0)]$ versus Zn concentration ($x=0.00$, 0.02, 0.03, and 0.05). Solid lines are drawn as a guide to the eye. For $x=0.00$ we have used the value of $\lambda_{ab}(0)$ for the CuO_2 planes (see text).

pected for a weak coupling BCS s-wave superconductor.[18]) This result was found in a previous study using different samples of the same Zn content which were aligned in wax.[10] It is probably mainly because 5% Zn (7.5% of the planar Cu atoms) smears out the anisotropy of the d-wave gap. However, as discussed below, Zn substitution also increases the c-axis coupling slightly and probably increases the superconducting coherence lengths in all directions via the effect on T_c.

The probable effect of Zn doping on the superfluid density (n_s) has been analyzed by using published specific heat,[4] NMR[8] and Gd^{3+} ESR[19] results which give consistent values for the residual density of states at the Fermi energy in the superconducting state.[19] We assume that this residual density of states (N_R) corresponds to unpaired electrons and therefore, plot our values of $\lambda_{ab}{}^2(0)$ and $\lambda_c{}^2(0)$ versus $1/N_S$, where in our notation $N_S=N_T-N_R$, N_T is the total density of states and (N_R/N_T) is given in Ref. 19. As shown in Fig. 4(a), $\lambda_{ab}{}^2(0)$ increases linearly with $1/N_S$, except for the $x=0.00$ sample where the deviation possibly arises from the chain contribution to $\lambda_{ab}(0)$.[20] From this deviation we estimate the value of $\lambda_{ab}(0)$ from the CuO_2 planes to be 1870 Å. [Note that plots of $[1/\lambda_{ab}(0)]^2$ versus N_S show that 0.02 or more Zn removes the Cu-O chain contribution to the superfluid density in agreement with our analysis of Fig. 4(a).] The values of $\lambda_c{}^2(0)$ do not increase linearly with $1/N_S$. This is probably due to a decrease in anisotropy with Zn doping as has also been found from resistivity studies for Zn doped $Bi_2Sr_2CaCu_2O_{8+y}$ crystals.[21] As shown in Fig. 4(b), $[\lambda_c(0)/\lambda_{ab}(0)]$ decreases linearly with Zn content [here we use the CuO_2 plane value for $\lambda_{ab}(0)$ derived above]. It has been suggested that the c-axis coupling in the cuprates is influenced by the $4s$ electrons of the in-plane Cu atoms,[17] which is possibly consistent with our finding that Zn substitution increases the c-axis coupling (of course there is a net increase in λ_c because the superfluid density is reduced by Zn doping). As discussed below this relatively small increase in c-axis coupling combined with the strong reduction in T_c leads to a larger superconducting coherence length $[\xi_c(T)]$ in the c direction and fluctuation effects near T_c should be reduced.

The ratio $[\lambda_c(0)/\lambda_{ab}(0)]$ falls to the relatively small value of 4.4 at $x=0.05$. We have checked the original formulae relating $\chi(H_{ac}\|ab)$ and λ_c in both the large[22,23] and small[24] grain limits to make sure that the relation $\lambda_c=1.4\lambda_{\rm eff}$ (Ref. 10) remains valid. Here $\lambda_{\rm eff}$ is the effective penetration depth. It turns out that any error from this source is negligible ($<2.5\%$).

Finally, we discuss the kinks seen in $[1/\lambda_{ab}(T)]^2$ and $[1/\lambda_c(T)]^2$ for $x=0.00$ near T_c [Figs. 1(a) and 1(b)]. The kinks may be caused by superconducting fluctuations. When the coupling between CuO_2 planes within a unit cell is stronger than that between cells, a 2D-3D crossover in YBCO is expected at a reduced temperature $r=[2\xi_c{}^2(0)/d^2]=0.06$,[25] i.e., $T/T_c\approx 0.94$ which is close to where the kinks

are seen (Fig. 1). Here $\xi_c(0)$ is the c-axis coherence length [2 Å for YBCO (Ref. 26)] and d is the c-axis parameter [11.7 Å for YBCO (Ref. 27)]. However, as shown in Fig. 1 this kink is not detected for $x \geqslant 0.02$. From the values of T_c and the changes in anisotropy discussed above we would expect $r = 0.11$ for 0.02 Zn that is, a kink near 66 K in Fig. 1. It is perhaps possible that superconducting fluctuations are smeared out by 0.02 Zn. However, it is also noted that for $x = 0.00$, specific heat data on several fully oxygenated YBCO samples showed a substantial splitting of the anomaly at T_c.[4,28,29] This splitting was suppressed by $x = 0.02$ Zn,[4] oxygen deficiency[28] or Co substitution.[29] It therefore seems likely that the kink near T_c for $x = 0.00$ could be a subtle manifestation of chain superconductivity rather than a straightforward fluctuation effect.

In summary, we have investigated the dependences of the anisotropic magnetic penetration depth of high-quality grain-aligned YBCO on Zn doping and temperature. The values of $\lambda_{ab}(0)$ and $\lambda_c(0)$ were found to increase systematically with Zn doping. The observed increase in the values of $\lambda_{ab}(0)$ with Zn content is consistent with the residual density of states determined by other measurements. In contrast, the values of $\lambda_c(0)$ do not increase as quickly, probably because of a moderate increase in the c-axis coupling strength. Below ~ 25 K $\lambda_{ab}(T)$ and $\lambda_c(T)$ for pure YBCO obey a linear T power law characteristic of d-wave superconductivity. These linear T dependences change to T^2 with the addition of Zn ($x = 0.02$, 0.03, and 0.05). While $\lambda_{ab}(T)$ for $x = 0.00$ is consistent with a weak coupling d-wave model over the whole temperature range $\lambda_c(T)$ shows a flatter temperature dependence. However, for high Zn doping ($x = 0.05$) both quantities have essentially the same behavior.

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