High-precision penetration-depth measurement of $YBa_2Cu_3O_{7-\delta}$ as a function of oxygen content

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A mutual-inductance technique has been used for the high accuracy determination of the absolute London penetration depth in $YBa_2Cu_3O_{7-\delta}$ thin films. In order to study the influence of the CuO chains, the oxygen content has been varied in a wide range. At low temperatures the penetration depths obey power laws that depend on the sample but not at all on its oxygen depletion. This finding is best explained in terms of *d*-wave pairing with impurity scattering located in the CuO_2 planes. [S0163-1829(96)51922-3]

Although the high-temperature superconductors have been in the focus of intense research for many years, the underlying microscopic pairing mechanism has not been satisfactorily clarified yet. In this context the symmetry of the superconducting order parameter plays a key role in a full understanding, and there has been an ongoing discussion whether cuprate superconductors exhibit conventional or some kind of unconventional pairing. To distinguish between finite gap superconductivity and order parameters with nodes on the Fermi surface there are two independent approaches.

The classical way is to look for the density of low-lying electronic states which enters directly in such quantities as the electronic specific heat or the magnetic penetration depth $\lambda(T)$. The alternative way is to observe symmetry related changes in the sign of the wave function or its consequences for the transition matrices probed by scattering experiments. Both types of experiments have to complement each other to give a consistent and convincing picture.

In fact, in the latter case superconducting quantum interference device (SQUID) loop and electronic Raman experiments strongly favor *d*-wave superconductivity.[1–3] Measurements of the magnetic penetration depth have been performed by a variety of authors where some have claimed an exponential drop at low temperatures,[4] whereas others have observed power-law dependences[5–7] expected for gap functions with nodes on the Fermi surface.[8]

All these experiments were carried out using $YBa_2Cu_3O_{7-\delta}$ either in the form of single crystals or thin films. However, with respect to $YBa_2Cu_3O_{7-\delta}$ there is an additional complication on the interpretation of such data. It arises from the CuO chains which are coupled as a second conductive system to the superconducting CuO_2 planes. This coupling has been addressed by Kresin, Wolf, and Deutscher.[9] Taking into account proximity effect and phonon mediated tunneling they inferred that the chains should become superconducting, too. As a result, a double gap structure appears in the quasiparticle excitation spectrum where the chain gap is substantially smaller than the plane gap whose magnitude is correlated to the high transition temperature. In addition, the chain gap value is very sensitive to the oxygen content of $YBa_2Cu_3O_{7-\delta}$. On the one hand, the chain to plane distance is expanded with increasing oxygen depletion reducing the overlap of the electronic wave functions and the coupling strength. On the other hand, oxygen vacancies in the chains may lead to net magnetic moments at the copper chain sites acting as strong pairbreakers and giving rise to low-lying excitations. As a result the chain states rapidly become gapless even for moderate oxygen deficiencies around $\delta \approx 0.15$ and the temperature dependence of the penetration depth changes from an exponential to a power-law behavior, where the power is correlated to the oxygen content of the sample.[10,11]

Consequently, the observation of a power law can be interpreted either in terms of an unconventional pairing mechanism or in terms of a conventional *s*-wave superconductor coupled to the gapless, oxygen deficient CuO-chain system. To settle this controversy the theoretical predictions of the above model have to be checked by an evaluation of the $YBa_2Cu_3O_{7-\delta}$ penetration depth for various oxygen stoichiometries. According to Kresin and Wolf, the low-temperature behavior should depend extremely on the chain occupation factor and in the doping range of $0.1 < \delta < 0.2$ it is expected to change drastically.

To determine the temperature dependence of the penetration depth as a function of oxygen content we have chosen a mutual inductance technique similar to Fiory *et al.* where a superconducting film is placed between two flat coils stacked along a common *z* axis.[12] In principle this nondestructive method combines the advantages of the more generally used rf resonator and muon-spin-rotation (μSR) techniques—namely, high accuracy and the determination of the absolute $\lambda(T)$ value. To achieve highest precision, however, crosstalk of the coils has to be eliminated. In their original approach Fiory *et al.* used—at the expense of sensitivity—astatically wound coils of reduced dimensions (1 mm diam.). We simply suppress crosstalk completely by using the large screening area of films up to 4 inches in diameter. So we can retain larger coils (5 mm diam.) without astatic winding resulting in a much higher sensitivity. The primary coil is driven by a 30 kHz alternating current and the transmitted signal in the pick up coil is phase sensitively detected by a standard lock-in amplifier. A commercial Ge resistor close to the coils serves to record the temperature of the sample which can be varied between 2 and 300 K at a typical warm up rate of 0.2 K per minute. Data were taken every 0.1 K, so that the interesting low-temperature region ($T < 0.2\ T_c$) typically contains around 150 data points.

Due to the simple geometry and the short coherence length of $YBa_2Cu_3O_{7-\delta}$ which allows for local electrody-

namics the penetration depth can be calculated exactly on the basis of Maxwell's and London's equations. The mutual inductance of a pair of circular loops in the presence of the film can be found by expanding the vector potential into Bessel functions $J_1(kr)$ and solving the boundary conditions for each component. This results in

$$L_{12}=\pi\mu_0 r_1 r_2\int_0^\infty dk\ T(k)J_1(kr_1)J_1(kr_2)e^{-kD}. \quad (1)$$

Here, $J_1(kr_i)$ is the first-order Bessel function, r_i are the radii of the loops, and D their mutual distance in z direction. The transmission coefficient $T(k)$ is given by

$$T(k)=\frac{2}{2\cosh\left(\frac{d}{\lambda}\right)+\left(k\lambda+\frac{1}{k\lambda}\right)\sinh\left(\frac{d}{\lambda}\right)}, \quad (2)$$

where d and λ are the film thickness and penetration depth, respectively. A more general treatment of the problem can be found in the literature.[13,14] Summing over all pairs of loops in the two coils we obtain the voltage induced in the pickup coil from which the penetration depth can be extracted numerically. The only input parameters are the known film thickness and the coil geometries. Consequently, the accuracy of this simple, nondestructive measurement can be specified by $\delta\lambda=5$ Å in the absolute value and $\delta(\Delta\lambda)=0.5$ Å in the relative change of λ comparable to the highest precision achieved with resonator structures.

In order to avoid complication of the above analysis by penetrating flux vortices the driving field (typically $\approx$100 μT) is kept well below H_{c1} and the film remains in the Meissner state until T_c is closely approached. Frozen in flux, e.g., from earth's field, remains fixed and cannot respond to the ac modulation due to strong pinning forces. An independent check using a strong CoSm permanent magnet close to the coils resulted in a changed response above 70 K but left the low-temperature data unaffected confirming the strong pinning assumption.

For the present study we employed 200 nm thick, c-axis oriented, epitaxial $YBa_2Cu_3O_{7-\delta}$ films grown by thermal coevaporation on $LaAlO_3$ (2 inches) and YSZ (4 inches) substrates. The deposition procedure has been reported elsewhere and the quality of these films can be considered homogeneous over the whole film area.[15] Typically, as-grown films exhibit sharp transitions between 86 and 89 K and critical current densities $j_c(77\ \mathrm{K})>2\times10^6$ A/cm^2. To rule out gradual surface degradation the films were covered *in situ* by 40 nm thick Y_2O_3 capping layers. In a series of successive annealing steps the films were held at 480 °C for two hours under various oxygen atmospheres between 1 and 1000 mbar. After equilibration they were cooled to room temperature within 30 minutes at the same oxygen pressure applied during annealing. In this way the oxygen content of each sample could be varied in the range $0\leqslant\delta\leqslant0.6$. Following each annealing step the oxygen concentration has been determined by x-ray diffraction comparing the c-axis lattice parameter to published bulk values.[16] In any case the sharp inductive transitions ($\Delta T_c<1$ K) implied a homogeneous oxygen distribution throughout the entire film thickness. To check reversibility, in a final annealing step the oxygen depleted films were reloaded and we recovered T_c, λ_0, and the lattice parameter of the original as-grown state.

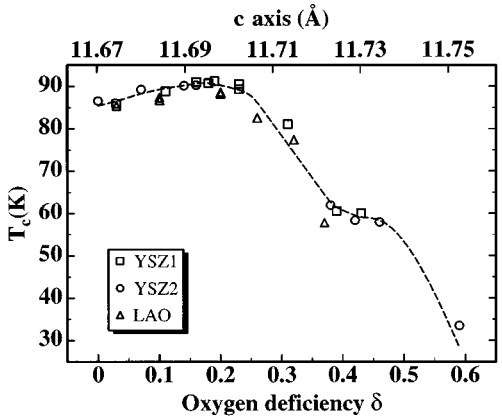

FIG. 1. Transition temperature as a function of oxygen depletion δ for three $YBa_2Cu_3O_{7-\delta}$ films on YSZ (circles, squares) and $LaAlO_3$ (triangles) substrates.

The change of the transition temperature upon reducing oxygen is depicted in Fig. 1 for three different samples. Since the c-axis length of thin films may differ from the bulk values the deduced absolute oxygen depletion δ may be slightly overestimated. Obviously, as-grown films are overdoped and reducing oxygen increases T_c beyond 90 K leading to a pronounced maximum around $\delta=0.15$–0.20. An analogous behavior has been observed in $YBa_2Cu_3O_{7-\delta}$ single crystals previously.[17] Upon further depletion the transition temperature sharply drops off to the well-established 60 K plateau.

Figure 2 shows the zero temperature penetration depth λ_0 (open symbols) and the extracted superconducting carrier density n_s (full symbols) for the same films as in Fig. 1. The carrier density has been deduced from

$$n_s(T=0)=\frac{m^*}{\mu_0\lambda_0^2e^2}, \quad (3)$$

where we assumed a constant effective mass $m^*=5m_e$.[18] In fact, the linear correlation between n_s and δ justifies this assumption. As-grown films exhibit the shortest penetration depth ($\lambda_0\approx145$–160 nm) and the highest carrier density.

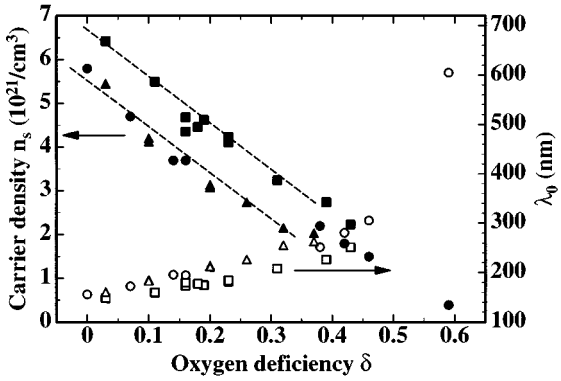

FIG. 2. Zero-temperature penetration depth (open symbols) and deduced superconducting carrier density (full symbols) vs oxygen depletion. Notation as in Fig. 1.

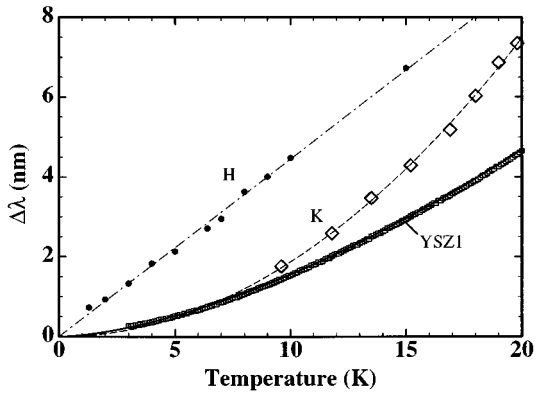

FIG. 3. Low-temperature penetration depth of fully oxygenated $YBa_2Cu_3O_{7-\delta}$ together with appropriate power-law fits (see text for details). In addition to our own data of the as-grown film YSZ1 (squares) data of Hardy *et al.* (●) (Ref. 7) and Klein (◇) (Ref. 4) have been added for comparison. Extrapolated λ_0 values have been extracted from the fits. The size of the symbols corresponds to the experimental error.

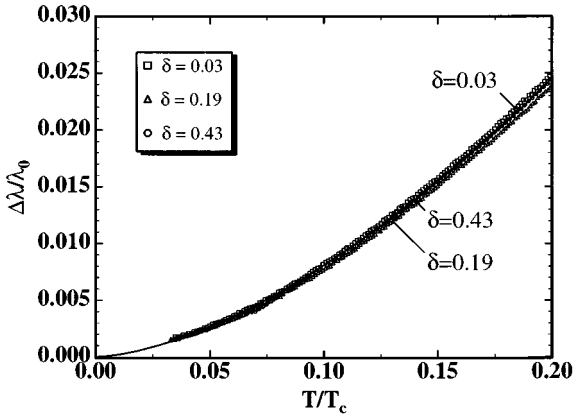

FIG. 4. Low-temperature penetration depth of the same $YBa_2Cu_3O_{7-\delta}$ film (YSZ1) with three different oxidation states ($\delta=0.03$, $\delta=0.43$, $\delta=0.19$ from top to bottom). The solid line indicates a power law fit with $\alpha=1.6$.

Comparison with Fig. 1 confirms again that there exists an overdoped regime ($\delta<0.15$) where T_c rises although the number of carriers decreases. In turn this implies that the CuO chains of our as-grown films are practically filled.

The low-temperature behavior of the penetration depth of such an as-grown film is depicted in Fig. 3 (open squares) together with literature data for samples claimed fully oxygenated.[4,7] The trace YSZ1 is representative for another 15 similar measurements on various films. In any case the low-temperature dependence could be perfectly fitted by a power law

$$\lambda(T)=\lambda_0+aT^{\alpha}. \tag{4}$$

Proper adjustment of the parameters λ_0, α, and a yields fits indistinguishable from the data points evident from the superimposed fit (solid line) with $\alpha=1.59$.

However, for different films the fit parameters scatter considerably indicating that they are not intrinsic. For instance, in all the samples measured so far the power α covers the range from 1.4 to 2.2, i.e., roughly between linear and quadratic. The fit parameters for the as-grown films introduced in Fig. 1 are listed in Table I for demonstration.

Power laws for λ(T) have also been observed by other authors. In thin films[5,6] and in doped single crystals,[19] a more or less quadratic dependence was found, while very pure single crystals are best described by a linear behavior.[7] For comparison, the latter data of Hardy *et al.* have been included into Fig. 3 (dots) together with a straight line (dashed-dotted line). We have also added penetration-depth data of the best film of Klein *et al.* (diamonds) which were originally interpreted in terms of an exponential BCS-type behavior $\Delta\lambda(T)\propto\sqrt{\Delta/k_BT}\exp(-\Delta/k_BT)$. In contrast, however, a quadratic fit (broken line) demonstrates that it is nearly impossible to decide the case on the basis of these data. It should be noted that there was no way to obtain satisfactory exponential fits to our data even when choosing very small gap values.

TABLE I. Transition temperatures and power-law fit parameters for the low-temperature penetration depth of three as-grown $YBa_2Cu_3O_{7-\delta}$ films.

Sample	T_c (K)	λ_0 (nm)	α	a (nm/K$^{\alpha}$)
YSZ1	86.4	147.6	1.59	0.040
YSZ2	86.6	156.1	1.87	0.015
LAO	85.4	161.7	1.98	0.010

The current interpretation of the observed power law is the assumption of an order parameter with nodes in k space, like d-wave pairing. For pure material, this should lead to a linear behavior,[8] while impurity scattering mixes k states of high and low gap directions, so that the density of low-lying states is altered and a more quadratic behavior results.[20–22] In light of this reasoning the increase of λ_0 and α in Table I demonstrates a varying impurity scattering from film to film which is certainly plausible since the cation stoichiometry may slightly differ. In this context it becomes obvious that the penetration depth is much more sensitive in addressing the question of sample quality than are T_c or j_c since in the latter respect the films are practically identical.

To consider the alternative interpretation of Kresin and Wolf and to elucidate the role of the chain oxygen, the low-temperature penetration depth ($T<0.2\ T_c$) is shown in Fig. 4 for one and the same sample with varying oxygen contents. For a direct comparison $\Delta\lambda/\lambda_0$, i.e., the quasiparticle fraction, has been plotted versus reduced temperature T/T_c. To avoid confusion by a bunch of overlapping curves we just picked three representative data sets of sample YSZ1 in three different oxidation states: film as grown ($\delta=0.03$), at maximum T_c ($\delta=0.19$) and in the 60 K plateau ($\delta=0.43$). Obviously, all three sets are nearly identical and can be perfectly fitted by a single power law with $\alpha=1.6$ and $a=4.1\times10^{-2}$ nm/K$^{\alpha}$, indicated by the solid line. The same holds true for the entire annealing series.

Obviously, the fraction of thermally activated quasiparticles scales with the reduced temperature. Hence, it seems that the only effect of the chain oxygen is to change the energy scale via the corresponding T_c. In contrast, Kresin and Wolf predict an extra pair-breaking effect at an increasing density of oxygen vacancies. As a consequence the finite proximity gap of the chains should disappear leading to a

crossover in the functional dependence from an exponential to a power law where the power is correlated to the oxygen deficiency. These predictions are clearly not in agreement with our data.

Having demonstrated above that the penetration depth is extremely sensitive to small changes in the defect density it is all the more surprising that even massive oxygen depletion does not contribute at all to a variation of the scattering. The only likely explanation is that chain vacancies are much less efficient scatterers than defects within the CuO_2 planes.

In summary we have presented a nondestructive precision measurement of the absolute value of the magnetic penetration depth of thin films. Applying an appropriate annealing procedure we were able to vary the oxygen content of $YBa_2Cu_3O_{7-\delta}$ over a wide range. It turned out that films as grown by coevaporation were initially overdoped resulting in a slightly reduced transition temperature.

At low temperatures the penetration depth obeys a power law where the exponent depends on the sample but not at all on its oxygen content. This is in striking contrast to the predictions of the theory of coupled conventional *s*-wave superconductors put forward by Kresin and Wolf.[9–11] Instead, our results are best explained in terms of *d*-wave pairing combined with a scattering mechanism predominantly located in the CuO_2 planes. However, it should be noted that with respect to the *d*-wave picture it is still an open question why the λ_0 values reported for films and single crystals are equal in size although the latter are believed to contain orders of magnitude less defects. In our mind, this problem is certainly worthy of discussion in future papers.

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