Magnetic penetration depth and surface resistance in ultrahigh-purity $YBa_2Cu_3O_{7-\delta}$ crystals

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We have succeeded in growing very high-purity (99.995%) $YBa_2Cu_3O_{7-\delta}$ crystals in $BaZrO_3$ crucibles and have measured $\Delta\lambda(T)$ and $R_s(T)$ at 1 GHz in crystals with various oxygen treatments. For an oxygen vacancy level of $\delta=0.007$, $\Delta\lambda$ and R_s essentially reproduce our previous results and show no sign of the existence of the two order parameter components as recently reported by Srikanth *et al.* on $BaZrO_3$-grown crystals. For other oxygen concentrations, we have in some cases observed deviations from the linear low T dependence of $\Delta\lambda$, but never any sign of a second transition. [S0163-1829(98)50538-3]

Measurements of the electrodynamics of high temperature superconductors (high-T_c) have played a crucial role in understanding the physics of these materials. The temperature dependence of magnetic penetration depth $\lambda(T)$ and microwave surface resistance $R_s(T)$ gives information about the nature of quasiparticle excitations, their dynamics and, indirectly, information on the structure of the gap function. However, many early attempts at measuring these quantities led to misleading conclusions, partly because of problems with sample quality. The first concern is purity: impurities can be introduced into the high-T_c material either from the starting chemicals or from the crucible during crystal growth. The second concern is the quality of the surface. Since electrodynamic measurements involve probe currents that flow only within about a thousand angstroms of the surface of the crystal, it is natural to raise this concern, and one must make sure that measurements such as microwave surface impedance are consistent with bulk measurements such as specific heat or thermal conductivity.

The linear temperature dependence of $\lambda(T)$ was first observed by Hardy *et al.* for $YBa_2Cu_3O_{7-\delta}$ crystals grown in yttria stabilized zirconia (YSZ) crucibles (purity $\simeq$99.9%).[1] They found that $\Delta\lambda(T)=\lambda(T)-\lambda(1.2\text{ K})$ below 20 K is largely linear with a slight, sample-dependent curvature below 4 or 5 K. Furthermore, studies of deliberate cation substitutions revealed that the penetration depth is very sensitive to certain types of impurities: for example, 0.3% Zn is enough to change the low temperature behavior from linear to quadratic. Other types of crystal defects might have a similar effect; in particular, most films exhibit a T^2 behavior. It was therefore reasonable to believe that the observed sample variation in YSZ-grown pure crystals was due to the presence of impurities or other crystal imperfections.

Similar conclusions were drawn concerning the surface resistance of $YBa_2Cu_3O_{7-\delta}$ single crystals. Bonn *et al.* observed a peak in $R_s(T)$ of YSZ-grown crystals below T_c which was attributed to a rapid increase in quasiparticle scattering time in the superconducting state.[2] However, the magnitude of the increase could be limited by deliberately introducing impurities: 0.3% Zn and 0.7% Ni were shown to be enough to completely suppress the peak. This left open the question of whether or not the scattering time at low temperatures in YSZ-grown crystals is limited by the residual 0.1% impurities, or by some other mechanism. Like $\lambda(T)$, $R_s(T)$ also exhibits considerable sample dependence below 4 K. The magnitude of the residual $R_s(T)$ at 1.2 K varies considerably and the temperature dependence of $R_s(T)$ at low T varies from linear to quadratic.[3] These all point to the fact that the presence of residual impurities and crystal defects prevents us from observing some important features of the intrinsic behavior of $YBa_2Cu_3O_{7-\delta}$.

A breakthrough in quality of $YBa_2Cu_3O_{7-\delta}$ crystals has been made through the use of $BaZrO_3$ crucibles instead of YSZ. Unlike YSZ, the $BaZrO_3$ crucibles are essentially inert and do not add measurable impurities to the melt during the growth process. This results in crystals with at least one order of magnitude increase in purity as well as higher crystallinity. Erb *et al.* were the first group to grow such crystals[4] and Srikanth *et al.* have performed microwave measurements on them.[5] Recently Ruixing Liang in our group at UBC has succeeded in fabricating $BaZrO_3$ crucibles and growing high-purity crystals in them. In this paper we present the results of our first series of measurements of the microwave surface impedance of this generation of crystals.

The $YBa_2Cu_3O_{7-\delta}$ crystals are grown by a flux-growth technique in $BaZrO_3$ crucibles. Details of the fabrication of the crucibles and the crystal growth are given elsewhere.[6] The crystals have not only high chemical purity (99.99–99.995%), but also a high degree of crystalline perfection as measured by the width of the (006) rocking curve, FWHM $=0.007°$ (including 0.003° instrumental resolution), a factor of 3 better than the YSZ-grown crystals. The surface impedance measurements are performed using a superconducting loop gap resonator operating at 1.1 GHz. The sample is positioned inside the loop such that the rf field is applied parallel to the ab plane of the crystal. This way the currents flow primarily in the ab plane, with a small contribution from the c-axis currents. In previous studies, we have separated out the c-axis contribution to $\lambda(T)$[7] and most recently have done so for $R_s(T)$.[8] However, in this paper we ignore c-axis contributions, which introduce errors of less than 5% to the results and will not affect qualitative features of the temperature dependencies.

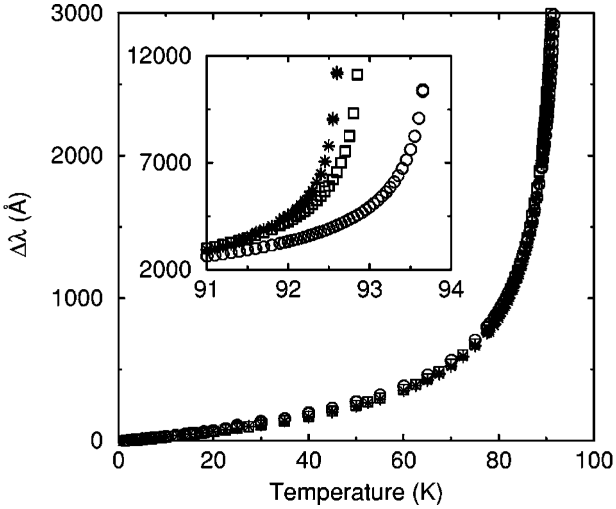

FIG. 1. $\Delta\lambda(T)$ vs T for twinned crystals of $YBa_2Cu_3O_{7-\delta}$ grown in $BaZrO_3$ crucibles with various annealing temperatures, 500 °C (circle), 475 °C (square), and 450° C (star). Inset shows the variation of T_c with annealing temperature.

In an attempt to determine optimal conditions for oxygen doping, we have measured $\Delta\lambda(T)$ for three crystals annealed in flowing oxygen at temperatures ranging from 450 to 500 °C. The areas of the crystals vary between 0.5 to 4 mm^2 with thicknesses of 25 to 55 microns. The data for all three samples shown in Fig. 1 are similar, with no indication of the second-order parameter component reported by Srikanth *et al.*[5] The inset shows the variation of T_c with annealing temperature, with the highest T_c of 93.7 K achieved by annealing at 500 °C.

The same data, shown in detail below 20 K in Fig. 2, exhibits curvature which differs from the largely linear dependencies observed for YSZ-grown crystals. A possible explanation is that the chain oxygen vacancies in the higher purity $BaZrO_3$-grown crystals have a tendency to cluster. Erb *et al.*[9] have proposed that ''fishtail''-shaped magnetization loops observed in their optimally doped crystals (and in ours) are in fact due to pinning by the vacancy clusters. Whatever these defects ultimately turn out to be, they could act as electronic scattering centers, thus moving $\Delta\lambda(T)$ towards the quadratic temperature dependence observed in Zn-doped samples.[2]

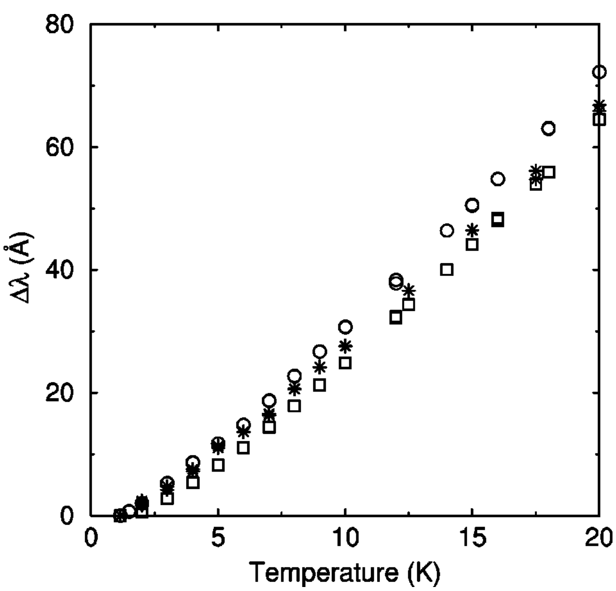

FIG. 2. Same data as in Fig. 1 shown below 20 K.

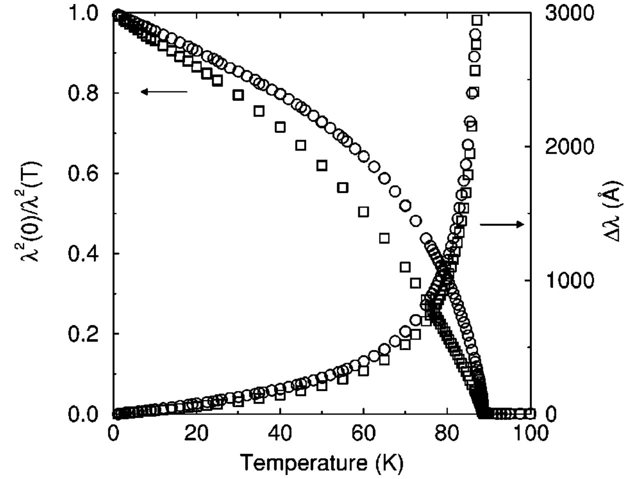

FIG. 3. $\Delta\lambda(T)$ vs T (right-hand axis) and superfluid fraction $\lambda^2(0)/\lambda^2(T)$ vs T (left-hand axis) for a detwinned crystal of $YBa_2Cu_3O_{6.993}$, for a (circle) and b (square) directions.

One obvious way to avoid the clustering posited by Erb *et al.* is to dope the crystals as close as possible to O_7, where it has been shown that the magnetization ''fishtail'' disappears.[10] Figures 3 and 4 show the results of this approach. The crystals were detwinned and then annealed for 50 days, with the annealing temperature initially set at 450 °C and then decreased in several steps, the last one being 350 °C which corresponds to $O_{6.993}$. Figure 3 shows $\Delta\lambda(T)$ and the superfluid fraction $\lambda^2(0)/\lambda^2(T)$ for the a and b directions over the whole temperature range below $T_c \simeq 88.7$ K. The $\Delta\lambda$'s are similar to those shown in Fig. 1 and do not differ substantially from data on crystals grown in YSZ crucibles. As yet, the zero temperature values of penetration depth, $\lambda(0)$, of these crystals are not known. We have used values $\lambda_a(0) = 1600$ Å and $\lambda_b(0) = 800$ Å which are inferred from muon spin relaxation measurements for

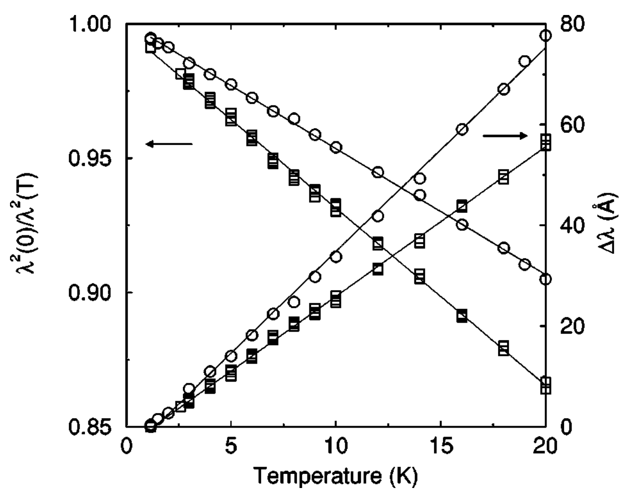

FIG. 4. Same as Fig. 3 but shown for below 20 K. All solid lines are linear fits to the data.

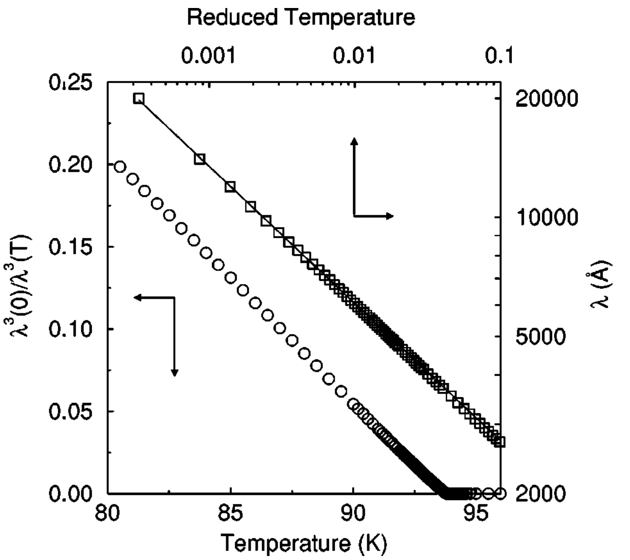

FIG. 5. 3D *XY* critical behavior of the superfluid density in the superconducting state of a sample annealed to $YBa_2Cu_3O_{6.92}$. The circles show $\lambda^3(0)/\lambda^3(T)$ vs T (left and bottom axes) and the squares show $\lambda(t)$ vs reduced temperature $t=1-T/T_c$ on a log-log scale (right and top axes).

overdoped $YBa_2Cu_3O_{7-\delta}$ crystals.[11] However, the choice of λ(0) does not affect the qualitative features of the superfluid density, namely no signature of a second-order parameter component developing below T_c as reported by Srikanth *et al.*, and nonmean field behavior near T_c.

Figure 4 shows the detailed behavior of the data below 20 K, revealing a slight curvature in Δλ in the *a* direction and very linear temperature dependence in the *b* direction. Linear fits to $\Delta\lambda(T)$ give slopes of 4.0 Å/K and 3.0 Å/K for the *a* and *b* directions, respectively, which are very similar to the slopes of 4.0 Å/K and 3.2 Å/K observed for overdoped $YBa_2Cu_3O_{7-\delta}$ crystals grown in YSZ crucibles. Power law fits to $\lambda^2(0)/\lambda^2(T)$ below 20 K give exponents of 1.06 and 0.94 for the *a* and *b* directions, respectively, very close to linear.

We call attention to the fact that the linear temperature dependence persists down to the 1.15 K base temperature, whereas for YSZ-grown crystals we typically observe a crossover towards higher power laws below 4 or 5 K. This supports the conjecture that the curvature observed in YSZ-grown crystals is due to the presence of the ~0.1% impurities: the new crystals have more than an order of magnitude higher purity and correspondingly little curvature. Kosztin and Leggett[12] have predicted that nonlocal effects can result in deviations from the expected linear temperature dependencies even for a pure *d*-wave superconductor. However, as they have noted, nonlocal effects for the *ab* plane penetration depth are mainly important in the geometry where the magnetic field is applied parallel to the *c* axis. In the measurements reported here, the rf field is applied parallel to the *ab* plane and nonlocal effects should be negligible.

Previous measurements of $\lambda(T)$ in our laboratory have shown nonmean field behavior close to T_c. Kamal *et al.* observed that in YSZ-grown crystals, the superfluid density shows the critical behavior of the three-dimensional (3D) *XY* universality class and that, surprisingly, the critical region is as wide as 10 K.[13] In Fig. 5 we show $\lambda^3(0)/\lambda^3(T)$ (circles) for a twinned $BaZrO_3$-grown $YBa_2Cu_3O_{7-\delta}$ single crystal. The crystal was annealed at 500 °C to an oxygen content of $O_{6.92}$, which yields the maximum possible T_c (93.78 K), the sharpest transition (0.25 K), and thus the clearest data near T_c. Other oxygen contents show similar behavior near T_c, but with slightly broader transitions. For λ(0) we have chosen 1400 Å, the same value used for twinned, YSZ-grown crystals, but again the results are not very sensitive to this value. As seen in the figure, this crystal also shows 3D *XY* critical fluctuations over a fairly wide temperature range, ~10 K, very similar to YSZ-grown crystals. The squares show a log-log plot of λ as a function of reduced temperature, $t=1-T/T_c$. The solid line is a fit to a power law $\lambda(t)\propto t^{-y}$ with $y=0.34\pm.01$, where the error corresponds to assuming ±200 Å error in λ(0). This exponent agrees with the 3D *XY* critical exponent $\nu/2=1/3$.

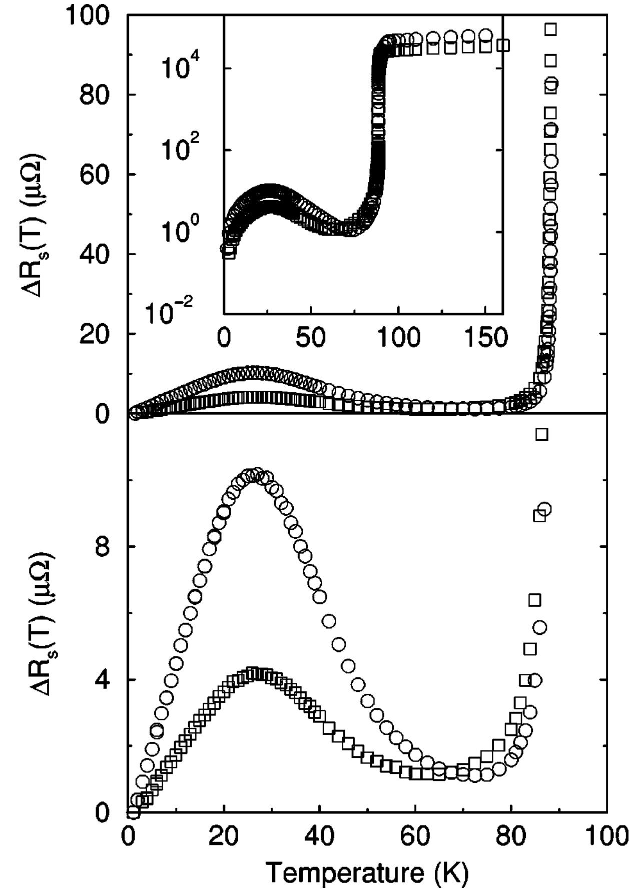

FIG. 6. Surface resistance vs T for the same detwinned crystal of $YBa_2Cu_3O_{6.993}$ used for Figs. 3 and 4, for *a* (circle) and *b* (square) directions.

The loop gap resonator and sample holder used in these measurements were designed mainly for precision measurements of $\lambda(T)$. However, we have recently succeeded in making simultaneous measurements of surface resistance using this resonator, thanks to recent improvements in the unloaded Q ($Q_0 \simeq 4\times10^6$) and to the use of time domain techniques. In our surface resistance measurements we are usually able to withdraw the sample from the resonator in order to find the unloaded Q. This is not possible in the present configuration and we can only measure the change of surface resistance, $\Delta R_s(T)=R_s(T)-R_s(1.15\text{ K})$.

Figure 6 shows $\Delta R_s(T)$ for the same detwinned, overdoped crystal used for Figs. 3 and 4. The main features are similar to our previous results on crystals grown in YSZ crucibles, where the peak at 26 K is attributed to a rapid rise in the quasiparticle scattering time below T_c. In particular, there is no indication whatsoever of a second-order parameter developing below T_c as reported by Srikanth *et al.*[5] One of the striking features of the data is that the average rise in R_s from its minimum at about 70 K to its maximum at 26 K is roughly fourfold compared to the twofold increase in crystals from YSZ crucibles. We interpret this as indicating that in the new crystals the quasiparticle scattering time rises to a much higher limiting value than in the YSZ-grown crystals, a consequence of the higher purity of the $BaZrO_3$-grown crystals. Another noteworthy difference is that $R_s(T)$ varies linearly with temperature all the way down to 1.15 K, with slopes of 0.52 and 0.21 $\mu\Omega$/K for a and b directions, respectively.

In summary, we have presented $\Delta\lambda(T)$ and $R_s(T)$ for very high-purity crystals of $YBa_2Cu_3O_{7-\delta}$ grown in $BaZrO_3$ crucibles. The results show no evidence for two order parameter components. This is consistent with the fact that the specific heat of $BaZrO_3$-grown crystals produced by Erb, Walker, and Flükiger[10] exhibits a peak at T_c that is identical in size and shape to those seen in high quality YSZ-grown crystals.[14] The specific heat data on the new crystals also show no sign of a second superconducting phase transition. It is difficult to reconcile this *bulk* measurement on the $BaZrO_3$ crystals with the surface impedance data of Srikanth *et al.*[5] which shows a rather weak increase in the superfluid density near T_c and a new feature at lower temperatures.

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