Precision Measurements of the Temperature Dependence of λ in $YBa_2Cu_3O_{6.95}$: Strong Evidence for Nodes in the Gap Function

W. N. Hardy, D. A. Bonn, D. C. Morgan, Ruixing Liang, and Kuan Zhang
Department of Physics, University of British Columbia, Vancouver, British Columbia, Canada V6T 1Z1
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A miniature superconducting resonator operating at 1.3 K and 900 MHz has been used to measure the change in $\lambda(T)$ from 1.3 K to T_c in very high quality single crystals of $YBa_2Cu_3O_{6.95}$. The data, which have a resolution of 1–2 Å, show a strong linear term extending from approximately 3 to 25 K. We believe the strong linear dependence to be characteristic of the pure system and that its apparent absence in thin films and some crystals is due to the presence of defects.

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One of the central points of interest in the study of high T_c superconductors is the possibility that the superconducting state is something other than the conventional s-wave BCS pairing state. The energy gap in the excitation spectrum of a BCS pairing state manifests itself in exponentially activated temperature dependences of a wide variety of dynamic and thermodynamic properties at low tempertaures. One of the most important of these is the temperature dependence of the London penetration depth, $\lambda(T)$, at low temperatures which reflects changes in the superfluid density responsible for the screening of electromagnetic fields. Microwave techniques for measuring $\lambda(T)$ most commonly measure the temperature dependence of the deviation of $\lambda(T)$ from its zero temperature value, $\Delta\lambda(T) = \lambda(T) - \lambda(0)$. In s-wave BCS theory this quantity is given by [1]

$$\frac{\Delta\lambda(T)}{\lambda(0)} \sim 3.33 \left(\frac{T_c}{T}\right)^{1/2} \exp(-1.76T_c/T) . \quad (1)$$

The exponential term is a consequence of the energy gap, Δ, which takes on the value $\Delta/k_BT_c = 1.76$ in weak coupling BCS theory. A number of other possible pairing states involve more complicated gap functions, such as gaps that are odd in frequency or $k - k_f$ [2]. In the context of heavy fermion and high T_c superconductors it has been suggested that the presence of strong antiferromagnetic spin fluctuations in the normal state might favor a BCS-like singlet pairing state but with nodes in the gap function, so-called d-wave superconductivity [3–6]. All of these unconventional pairing states have low energy excitations that can give temperature dependences different from the exponentially activated behavior of Eq. (1). For instance, for the case of a gap with nodes, Annett, Goldenfeld, and Renn [7] have shown that all of the possible non-s-wave singlet pairing states of a superconductor with tetragonal or orthorhombic symmetry and a Fermi surface that has spherical or cylindrical topology have line nodes in the gap that give rise to a linear temperature dependence in the penetration depth, $\Delta\lambda(T) \propto T$. Although this strong temperature dependence in general is easily differentiated experimentally from the behavior of Eq. (1), there are at least two defect-related effects that could mask it. In a d-wave pairing state impurity scattering can change the temperature dependence from T to T^2 [8–10]. Most precision measurements of $\Delta\lambda(T)$ have been performed on thin films [11–14] where a quadratic temperature dependence [7, 12–15] is often observed. The difficulty of attributing this quadratic behavior to the effect of scattering by defects in the films is that there should be a large suppression of T_c at the defect level required to produce a T^2 power law; but there are films that have a quadratic behavior without a suppressed T_c. A possible source of T^2 behavior that does not necessarily degrade T_c is the presence of weak links associated with grain boundaries in the films [16]. Whatever the explanation for the quadratic behavior observed in thin films, it is extremely important to attempt precision measurements of $\Delta\lambda$ on high quality single crystals where there are no grain boundaries and the impurity scattering can be much smaller than it is in films. Indeed, our recent measurements of the microwave loss of crystals of $YBa_2Cu_3O_{6.95}$ suggest that the presence of additional disorder in thin films substantially alters the microwave properties at low temperatures [15, 17].

Our crystals are grown by a flux method in zirconia crucibles and all tests indicate that they are of extremely high quality [18]. Crystals from all batches have $T_c > 93$ K and very sharp transitions in magnetization, resistivity, and specific heat ($\Delta T_c < 0.25$ K). The microwave loss, which is particularly sensitive to surface imperfections, shows extremely sharp transitions and low residual microwave loss. Although it would be preferable to work with untwinned crystals, we know that the microwave loss is very sensitive to mechanical damage. Therefore we have so far not used mechanically detwinned crystals.

The measurements of $\Delta\lambda(T) = \lambda(T) - \lambda(1.3\text{ K})$ reported here are made by a cavity perturbation method similar to the one we have used for microwave loss measurements in high T_c samples [19]. In that work the surface resistance, R_s, was measured from the change in Q of a superconducting microwave resonator when the sample, attached to a sapphire rod, was introduced through a hole in the microwave resonator into the microwave magnetic fields. In principle one can at the same time obtain $\lambda(T)$ from the absolute shift Δf of the resonator frequency. However, given that $\Delta f \simeq \kappa(a - \lambda)$, where κ is a geometrical constant and a is some appropriate dimension of the crystal, it is generally quite impractical

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to determine κ and a accurately enough to extract an absolute value for λ, when $a \gg \lambda$. In fact, for our standard configurations, because of systematic effects such as temperature related movement of the sample in the inhomogeneous electric fields, it is impossible to obtain reliable values even for the temperature dependence of λ. In order to measure λ well enough to be useful, we have found it necessary to develop a resonator specifically for the task of measuring frequency shifts rather than Q's.

The new cavity perturbation apparatus, which uses a split-ring type of resonator (shown in cross section in Fig. 2), was designed to suppress a number of systematic effects. The relatively low frequency of 900 MHz minimizes the electric fields that are present and also makes the sample loss negligible except very near T_c. Also, in order to minimize motion of the sample as its temperature is changed, the assembly that sustains the temperature gradient is made of quartz glass terminated by sapphire blocks. The sample itself is mounted flat on a thin sapphire plate having dimensions 17 mm × 3 mm × 0.1 mm using a very small amount of silicone grease. Finally, the main body of the resonator is kept in good contact with a temperature controlled helium bath, maintained at 1.3 K. The resonator is coupled weakly to both input and output coaxial lines. For the highest sensitivity, needed at the lowest temperatures, the system is run as a loop oscillator using room temperature electronics (amplifier, limiter, phase shifter, etc.). The Q of the resonator is typically 1×10^6 and a stability better than 1 Hz per minute can be achieved. For samples of broad dimensions $1.5 \times 1.5\,\mathrm{mm}^2$ this gave a resolution better than 1 Å in $\Delta\lambda$. At higher temperature, standard scalar transmission techniques are used which have a resolution somewhat worse than 1 Å but can be extended into the normal state where the oscillator technique no longer works.

If a crystal whose thickness, $2c$, is much less than its width and length is placed in the region of homogeneous magnetic field of a microwave cavity with the broad face parallel to the field, then the perturbations relative to no sample in the cavity are

$$\frac{\Delta f}{f} = \frac{1}{2}\frac{V_s}{V_r}\left[1 - \mathrm{Re}\left\{\frac{\tanh(\alpha c)}{\alpha c}\right\}\right], \qquad (2)$$

$$\Delta(1/Q) = \frac{V_s}{V_r}\,\mathrm{Im}\left\{\frac{\tanh(\alpha c)}{\alpha c}\right\}, \qquad (3)$$

where $\alpha = (1-i)/\delta$ for a metal (δ is the skin depth) and $\alpha = 1/\lambda$ for a superconductor at temperatures where the loss is negligible. Here V_s is the volume of the sample and V_r is the effective volume of the resonator (includes the filling factor). Defining $\delta f/f$ and $\delta(1/Q)$ to be values relative to the values for zero penetration into the sample we have $\delta(1/Q) = \Delta(1/Q)$ and $\delta f/f = \Delta f/f - V_s/2V_r$. In the limit $\delta \ll c$,

$$\frac{\delta f}{f} = -\frac{1}{4}\frac{V_s}{V_r}\frac{\delta}{c} \quad \text{(metallic case)}, \qquad (4)$$

$$\frac{\delta f}{f} = -\frac{1}{2}\frac{V_s}{V_r}\frac{\lambda}{c} \quad \text{(superconducting case)} \qquad (5)$$

(note the factor 2 difference in the two expressions).

Using these relations one can make an *in situ* determination of $V_s/(V_r c) = A_s/V_r$, where A_s is the area of the broad face of the sample: one compares δf in the normal state, where the skin depth can be determined from measurements of the dc resistivity, to the shift at 1.3 K where the difference between δf for $\lambda = 0$ to that for the actual $\lambda(0)$ can be neglected. We have performed a measurement with a reference sample of the superconductor $Pb_{0.95}Sn_{0.05}$ that was cut to the same dimensions as the $YBa_2Cu_3O_{6.95}$ crystal discussed below. The calibration factors for other crystals are then determined by the values of A_s relative to this reference sample.

The measurements of $\Delta\lambda$ for the $Pb_{0.95}Sn_{0.05}$ are presented in Fig. 1. The very weak temperature dependence below 2.5 K (T_c is 7.2 K) is consistent with s-wave BCS theory where $\Delta\lambda$ tends to be rather flat below $0.4T_c$. When the measurements shown in Fig. 1 are analyzed according to Eq. (1), but allowing for a gap ratio other than the weak coupling value, a clear exponential behavior is observed that corresponds to a strong coupling gap ratio of $\Delta/k_BT_c = 2.44 \pm 0.06$. Although this large gap ratio means that the data over the full range of temperatures below T_c should be compared to numerical calculations based on strong coupling theory, the fit to the low temperature data is close to the known gap ratio of $\Delta/k_BT_c = 2.25$ for pure Pb [20]. The success of this measurement of a conventional superconductor is a stringent test of the sensitivity of this technique since the unusual behavior of $\Delta\lambda$ presented below for $YBa_2Cu_3O_{6.95}$ involves larger values of $\Delta\lambda$.

Other checks for systematic errors included temperature ramps with no sapphire plate, sapphire plate with no sample, and the use of a Cu reference sample cut to the same dimensions as the $YBa_2Cu_3O_{6.95}$ crystal. The most difficult effect to check for, namely, frequency shifts

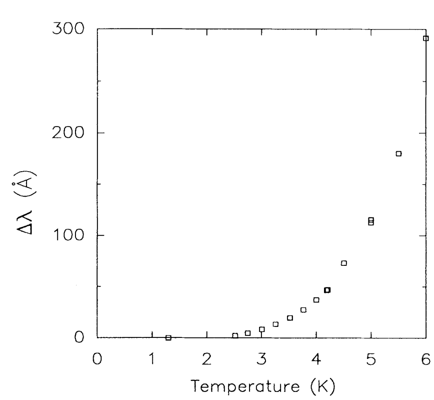

FIG. 1. The temperature dependence of $\Delta\lambda(T) = \lambda(T) - \lambda(0)$ for $Pb_{0.95}Sn_{0.05}$. The very weak temperature dependence below 2.5 K ($\approx 0.4T_c$) is characteristic of an s-wave superconductor with an energy gap.

due to a temperature dependence of the position of the sample in the not perfectly homogeneous magnetic field of the resonator, were shown to be negligible by taking measurements in increasingly inhomogeneous parts of the resonator. To the level of a few angstroms there are no systematic errors up to about 20 K. By 60 K there may be errors of order 10 Å which above 80 K are negligible compared to the effects being measured. Thermal expansion of the crystals [21], which gives a contribution $\delta f \propto \delta V/V$, becomes noticeable for thick crystals [22]. The data presented here come from a crystal that is thin enough that such effects can be ignored.

We have chosen to orient the *a-b* plane of the sample parallel to $\mathbf{H}_1$, the microwave magnetic field, in order to minimize the temperature independent part of the frequency shift. This of course brings in λ_c in addition to $\lambda_{a,b}$ since roughly $\delta f = f(T) - f(T_0) \propto (a\Delta\lambda_{a,b} + c\Delta\lambda_c)$, where a and c are the appropriate dimensions of the sample perpendicular to $\mathbf{H}_1$. We have checked the degree to which the results are contaminated by a contribution from $\Delta\lambda_c$ by measuring samples with different aspect ratios. The results shown in Fig. 2 are from a thin sample with an aspect ratio of $a/c \approx 100$. The thickest crystal that we have measured had an aspect ratio of 30 and exhibited similar temperature dependence, but with an absolute value roughly 10% larger. This small dependence on aspect ratio indicates that the measurements made on thin crystals are not contaminated by a large $\Delta\lambda_c$ and for the purposes of this paper it is reasonable to ignore the effects of λ_c.

Figure 2 shows $\Delta\lambda = \lambda(T) - \lambda(1.3\text{ K})$ for a crystal with dimensions 1.16×1.66 mm^2. To within the multiplicative calibration constant this is the raw data. The linear term, shown in more detail in Fig. 3, has a slope of 4.3 Å/K, and is essentially the same in all four crystals that have been measured. This linear behavior is what one expects for a clean *d*-wave superconductor with line nodes, for example, nodes in the k_z direction along the quasi-cylindrical Fermi surface expected for these anisotropic materials. The question immediately arises: Why has a strong linear term not been previously observed in $YBa_2Cu_3O_{7-\delta}$? We believe that this is due to the presence of defects in the thin films that are used for most of the precision measurements of $\lambda(T) - \lambda(0)$. In a multielement material, thin films are more likely to have substitutional and growth defects than single crystals. Arberg, Mansor, and Carbotte [10] have shown that impurity scattering in a 2D *d*-wave superconductor changes the temperature dependence of $\lambda(T) - \lambda(0)$ from a T to a T^2 power law at low temperatures and a power law close to T^2 is in fact what is observed in many high T_c films [7, 12–15]. However, the level of impurities required to completely suppress the linear term should also decrease T_c substantially, whereas some of the films that exhibit quadratic behavior have T_c's over 90 K. An alternative explanation for the behavior of $\Delta\lambda(T)$ in thin films might be enhanced penetration associated with grain boundaries [16]. The low field dc magnetization measurements of Krusin-Elbaum *et al.* [23] were performed on single crystals, but the signal to noise ratio in these earlier measurements was too low to clearly observe the linear term presented here and their crystals had a T_c of 89.7 K which indicates a relatively high level of impurities. Recent magnetization measurements provide evidence for non-*s*-wave behavior of the penetration depth in single crystals of $Tl_2Ba_2CaCu_2O_{8-y}$ [24].

It is useful to construct the quantity $[\lambda(0)/\lambda(T)]^2$ which one can identify with the normalized superfluid density n_s/n_0 and, in a generalized two-fluid model, deduce the normal fluid fraction $n_n/n_0 = 1 - [\lambda(0)/\lambda(T)]^2$. From the present experiment one obtains no information on the value of $\lambda(0)$ and we are forced to assume a value, guided by other experiments. Since our single crystal results do not agree with the thin film microwave data

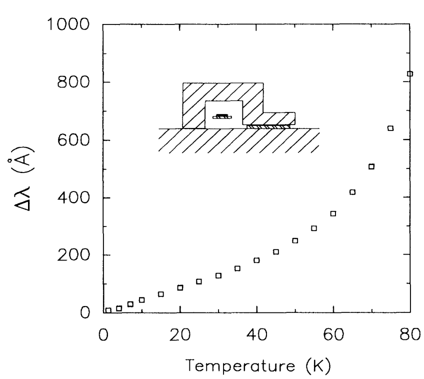

FIG. 2. The measured values of $\Delta\lambda_{ab} = \lambda(T) - \lambda(1.3\,\text{K})$ for a crystal of $YBa_2Cu_3O_{6.95}$. These measurements are presented over the same range of T/T_c as that used for $Pb_{0.95}Sn_{0.05}$ in Fig. 1 in order to highlight how much stronger the temperature dependence is than that found in a conventional superconductor. These results are essentially the raw frequency shift data obtained in the cavity microwave cavity configuration shown in the inset.

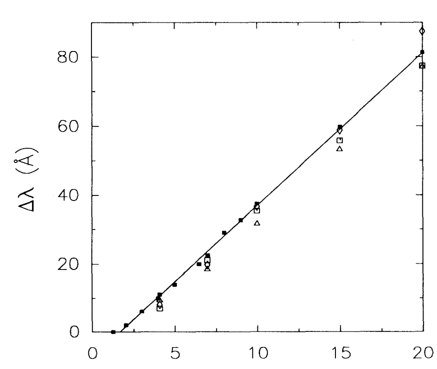

FIG. 3. A detailed view of $\Delta\lambda(T)$ in the low temperature limit where four different sets of data are all essentially linear in temperature with a slope of 4.3 Å/K. This strong linear term is what is expected for a superconductor with line nodes in the gap function.

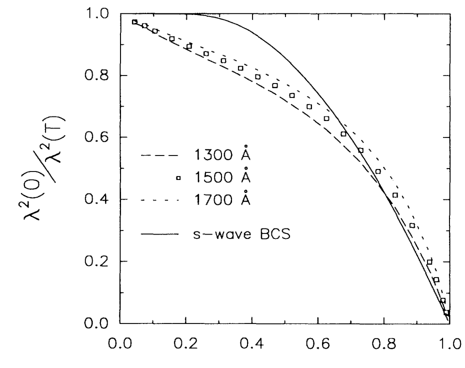

FIG. 4. The ratio $[\lambda(0)/\lambda(T)]^2$ extracted from the measurements of $\Delta\lambda(T)$ in a crystal of $YBa_2Cu_3O_{6.95}$ is a measure of the superfluid density. The different choices of $\lambda(0)$ (squares and long and short dashed curves) that are used have little effect on the overall shape and the strong linear behavior at low temperatures is clearly different from the *s*-wave BCS result.

(and we believe this to be a physical difference) and since the single crystal magnetization data have no model independent measure of $\lambda(0)$, there are no firm constraints provided by the low field data. High field muon-spin-rotation data [15] on crystals similar to the ones used here give an absolute value for $\lambda(0)$ of 1480 Å. However, if the nonlinear Meissner effect predicted for a *d*-wave superconductor [25] actually exists, one can imagine that the high field ($H \gg H_{c1}$) and low field ($H \ll H_{c1}$) effective values of $\lambda(0)$ need not be the same. In Fig. 4 we have plotted $[\lambda(0)/\lambda(T)]^2$ for a representative range of values of $\lambda(0)$: 1300, 1500, and 1700 Å. The overall shape of the curve is not much affected by the choice; a substantial linear term is always present at low temperatures and this is qualitatively different from the *s*-wave BCS result also shown in Fig. 4. Near T_c, the slope of the curve is roughly 3.8, which is substantially larger than that found for either *s*-wave or *d*-wave pairing in the weak coupling limit. Although it is possible that this is an indication of strong coupling effects [9], only the linear behavior at low temperature gives qualitative information about the pairing state that is essentially model independent.

In conclusion, we have observed a linear temperature dependence of $\Delta\lambda(T)$ below 20 K in single crystal $YBa_2Cu_3O_{6.95}$ that is very different from that expected for *s*-wave BCS superconductivity. It is also very different from the T^2 dependence that characterizes many of the precision microwave results for thin films. The linear temperature dependence is highly suggestive of line nodes in a clean *d*-wave superconductor. The T^2 term observed in thin films may be due to either the influence of point defects or extended defects such as grain boundaries. The exact cause of the behavior observed in thin films might be determined by further study of samples with controlled levels of defects.

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