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# Determination of the magnetic field penetration depth in superconducting yttrium barium copper oxide: Deviations from the Bardeen-Cooper-Schrieffer laws

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We have measured the low-field magnetization for a number of fine powders of $Y_1Ba_2Cu_3O_{7-\delta}$ and applied a standard formula to determine the magnetic field penetration depth $\lambda(T)$ in the superconducting state. Consistent values of $\lambda(0)$ and similar temperature dependences $\lambda(T)$ are obtained for average particle diameters ranging from 1.1 to 9 $\mu$m. At low temperatures $\lambda(T)$ is not Bardeen-Cooper-Schrieffer-like, instead a $T^2$ law is observed. The implications of this result are discussed.

The superconducting-state properties of the high-$T_c$ oxides have been investigated by a range of techniques. The average energy gap has been determined by tunneling and by optical methods, and the results are at present highly controversial.[1] Experiments which are sensitive to the normal electrons, such as specific heat or ultrasonic attenuation, are difficult because of the high transition temperatures, and surface impedance experments[2] give a distribution of gap values.

The measurement of the magnetic field penetration depth in the superconducting state $\lambda(T)$ has also been performed[3,4] using the technique of muon spin resonance. Two of the results[3] are in excellent agreement with the empirical law

$$\lambda(T)=\lambda(0)[1-(T/T_c)^4]^{-1/2}, \tag{1}$$

while a third[4] leads to drastic deviations for the above equation at low temperatures. Equation (1) has been found to describe the behavior of $\lambda$ for many ordinary superconductors. While there is no universal law for $\lambda(T/T_c)$ in the Bardeen-Cooper-Schrieffer (BCS) theory because its temperature dependence depends on the ratio of three quantities,[5] the zero-temperature coherence length $\xi_0$, the London penetration depth $\lambda_L(T)$, and the electronic mean-free path $l$, Eq. (1) corresponds to the weakest possible temperature dependence while in the local limit $\xi_0 \leq l \ll \lambda_L(T)$ a somewhat stronger temperature dependence, namely, $\lambda=\lambda_L(T/T_c)$, is expected.

The good agreement with Eq. (1) obtained in Ref. 3 was an important result because it seemed to rule out many unusual pairing mechanisms[3,6] and to narrow down considerably the possible theoretical descriptions of high-$T_c$ superconductivity.

In this paper we report a determination of $\lambda(T)$ by magnetic measurements on powder samples of $YBa_2Cu_3O_{7-\delta}$ with different particle sizes. We obtain $\lambda(0)$, and furthermore, we find that the temperature dependence of the penetration depth is anomalous. Below 40 K it follows a $T^2$ law similar to what was previously observed only for the heavy electron superconductor $UBe_{13}$.[7] It approximately follows the BCS law [i.e., the London penetration depth,[8] $\lambda_L(T/T_c)$] above 60 K.

The powder samples were prepared using an amorphous citrate process which has been referenced previously.[9] The first batch of samples ($D$ in Fig. 1) was fired at 900 °C for 10 h and then 950 °C for 1 h. The second ($A$, $B$, and $C$ in Fig. 1) was fired at 900 °C for 2 h. All batches were then annealed in air at 450 °C for 10 h and cooled at 1 °C per min to room temperature. X-ray powder diffraction showed that they were the correct single phase to within the detection limit of approximately 1%. Thermal gravimetric analysis for sample $D$ gave an oxygen content of $6.98 \pm 0.01$ (i.e., $\delta=0.02\pm0.01$).

Sample $D$ was prepared simply by passing the annealed powder through a 400-mesh sieve. Samples $A$, $B$, and $C$ were prepared by first passing the powder through a 400-mesh sieve and then separating out the finer particles ($A$ and $B$) by suspension in acetone. Their size distribution was determined using a "Micromeritics" particle-size analyzer based on the x-ray absorption of the particles

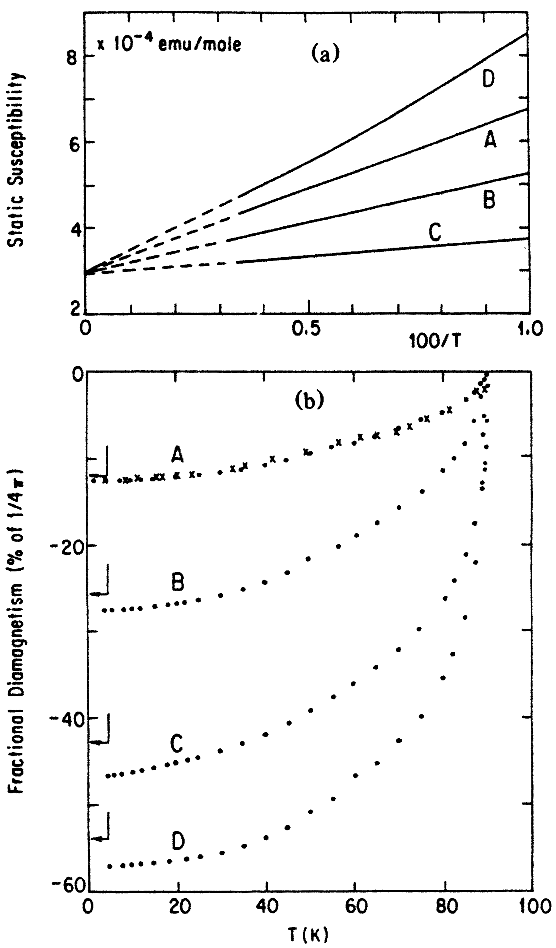


FIG. 1. (a) Static susceptibility data in the normal state. (b) Low-field ac magnetization for $Y_1Ba_2Cu_3O_7$ powders with different particle sizes expressed as a fraction of complete diamagnetic screening. The arrows show the values at 4.2 K obtained using the Faraday method and the crosses show static susceptibility data for sample *A* at 25 G.

during their sedimentation in a viscous liquid.

After separation, the powder samples were further characterized by measurements of magnetic susceptibility in the normal state at 9 kG using a Faraday balance.[10] Low-field magnetic measurements in the superconducting state were made using three independent methods. First, a low-frequency (LF) ac mutual inductance method was used with two identical sets of primary and secondary coils which was operated at 322 Hz with transformer amplification and lock-in detection. Second, a high-frequency (HF) single coil resonant method operating at 700 kHz was used with manual frequency sweep and lock-in detection of the resonance where the out-of-phase signal changed sign. In these cases the measuring field was normally 0.6 G peak to peak. For the LF method initial tests showed that increasing or decreasing the field by a factor of 10 did not alter the results. Thirdly, the Faraday balance was used with a static field of up to 25 G and a variable field gradient of up to 8 G/cm. All three of these methods gave essentially the same results, and the most complete data set was obtained for the LF method so these data are mainly reported here.

For the ac measurements the powder samples were contained in standard (number 5 size) gelatin drug capsules with a total volume of 0.138 $cm^3$. Care was taken to have good filling factors for the measuring coils. The two ac setups were calibrated using 100 $\mu$m niobium powder and various mixtures of this powder with alumina. The HF apparatus was also checked by measuring a copper ingot of the same shape as the capsule and the Faraday method by measuring a piece of superconducting lead.

Three of the coarser powder samples were mixed with alumina powder to give dilutions of 5–10 times by volume. These experiments showed that the effects observed were not associated either with screening currents flowing between particles or with possible magnetic interactions between them. This might be surprising at first sight; however, even the undiluted powders settled very loosely in the capsules, with volume ratios ranging from 0.38 for the coarsest to only 0.13 for the finest powders.

For the ac measurements gas flow or insertion cryostats were used and the samples were not evacuated before measurement, whereas in the Faraday measurements the sample space was pumped at $2\times10^{-5}$ Torr for several hours at room temperature.

Some typical magnetic data for various particle sizes are shown in Fig. 1. The upper part of the figure shows the static magnetic susceptibility in the normal state on a $1/T$ plot. It is important to note that all the curves have the same intercept at $1/T=0$, corresponding to a Pauli susceptibility of $3.0\pm0.1\times10^{-4}$ emu/mol. This is a good indication that the intrinsic electronic properties of our samples are independent of particle size. The lower part of the figure shows the LF ac magnetization data expressed as a fraction of the full diamagnetism corresponding to perfect shielding. In deriving the latter quantity we used the volume of the sample determined from its weight and the x-ray density of 6.36 g/cc. The ac data are in good agreement with the Faraday measurements taken at much higher fields (25 G). It can be seen that the various samples do have slightly different Curie terms in the normal state susceptibility. Differences between sample *D* and samples *A*, *B*, and *C* are probably due to the different heat treatments before annealing. Differences between *A*, *B*, and *C* may indicate that smaller particles have a larger fraction of paramagnetic centers. In any event these terms are relatively small, ranging from 2.1 to 16 mol% of $g=2$, $S=\frac{1}{2}$ spins, or 0.7 to 5.3% of the copper atoms. Subtraction of these Curie terms has negligible effect on the magnetization data in the superconducting state.

The measured particle-size distributions are shown in the upper part of Fig. 2. The diamagnetic screening at 4.2 K falls systematically as the average particle size decreases. For even larger particles (sample *E*, Table I), a maximum screening diamagnetism of 77% was observed which is comparable to that of our best sintered sample (81%).

Also shown in Fig. 2 is the distribution obtained from measurements of a scanning electron microscope photograph of sample *D*. Bearing in mind that it was a very limited region of the sample it is in satisfactory agreement with the x-ray method. Use of this distribution does not

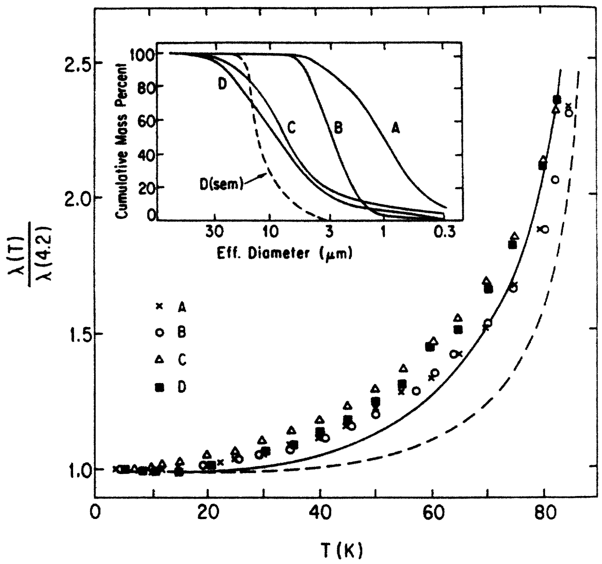


FIG. 2. Temperature dependence of the penetration depth $\lambda(T)$ vs temperature for the four types of powder. The solid line represents the London penetration depth $\lambda_L(T)$ (Ref. 9) and the dashed line the empirical law given by Eq. (1). These are the limiting forms which can be obtained for isotropic BCS superconductivity (Ref. 5). Inset, particle size distributions for the various samples measured.

alter the qualitative features of the results.

We used the formula given by Shoenberg[11] for the relative magnetization $M/M_{max}$ of a spherical superconductor, of radius $a$ with a magnetic field penetration depth $\lambda$:

$$M/M_{max} = 1 - 3x\coth\left(\frac{1}{x}\right) + 3x^2 \equiv F(x) , \qquad (2)$$

where $x = \lambda/a$. For $x < 0.02$, $F(x) \simeq 1 - 3x$; for $x > 4$, $F(x) \simeq 1/15x^2$.

This formula should hold well[12] for high-$T_c$ superconductors because of their short mean-free path[13] and short coherence length. Thus, using Eq. (2) (Ref. 14) together with the magnetization data in Fig. 1 and the particle size distributions in Fig. 2, we have computed values of $\lambda(T)$. No demagnetization factors were included in $M_{max}$ because the apparatus had been calibrated with niobium powder dispersed in alumina. The calculated values of $\lambda$ at 4.2 K are summarized in Table I. The four samples all give consistent values of $\lambda(0)$. The larger particle sizes tend to give slightly larger values. However, scanning electron micrographs show that the particles are not spherical but have a prismatic appearance. This would tend to increase the surface area/volume ratio leading to increased field penetration for small $\lambda/a$ values. It should be less important when $\lambda \approx a$ because the appropriate surface area is the one appearing on a length scale $\simeq \lambda$. We estimated possible uncertainties from this effect by making the drastic approximation that the particles were regular tetrahedra. For particles of the same volume the surface area/volume ratio is 50% larger for a tetrahedron. Since we also have data for $\lambda \approx a$ we believe that the values of $\lambda(0)$ in Table I cannot be more than approximately 25% too high.

As shown in Fig. 2 the temperature dependence of $\lambda(T)/\lambda(0)$ is approximately the same for all samples and is stronger than anything which can be obtained from BCS theory. As mentioned already, within BCS theory the strongest $T$ dependence $\lambda = \lambda_L(T)$ is obtained in the local limit and in most superconductors[5] a weaker dependence is obtained. The muon spin-resonance work[3] gives results which are in good agreement with the dashed line in Fig. 2 [i.e., Eq. (1) of the text], and a possible explanation for this discrepancy will be discussed later.

In Fig. 3 we show the low-temperature dependence of $\lambda(T)/\lambda(4.2\text{ K})$ on a $T^2$ plot. All samples obey a $T^2$ law up to about 40 K and three of them give consistent values for the slope. Shown also in Fig. 3 is the $T^2$ line observed[7] for the heavy-electron superconductor $UBe_{13}$, taking $\lambda(0) = 8000$ Å, and scaling the temperature scale by the appropriate ratio of the transition temperatures.

The value obtained for $\lambda(0)$ in the present work is $\lambda(0) = 0.62 \pm 0.03$ μm. In a free-electron model the value calculated from London's equation

$$\lambda_L^2 = \frac{mc^2}{4\pi ne^2} \qquad (3)$$

is $\lambda_L = 0.125$ μm, taking $n = 1$ carrier per $Y_1Ba_2Cu_3O_{7-\delta}$ formula unit and $m = m_e$ the free-electron mass. This value of $m$ follows from electron counting arguments with $\delta = 0$, i.e., $Y^{3+}$, $2Ba^{2+}$, $3Cu^{2+}$, and $7O^{2-}$.

There are several ways in which larger values of $\lambda$ could occur. If one uses the measured plasma frequency (Ref. 15) $\omega_p = 3$ eV/$\hbar$ to estimate $n/m$ then $\lambda = 0.4$ μm. In addition the effective mass could be enhanced by as much as a factor of 16 due to electron-electron interactions.[13] The role of electron mass renormalization on $\lambda$ is still the subject of research, but it could increase $\lambda$ by a factor of 4

TABLE I. Properties of the various $Y_1Ba_2Cu_3O_7$ samples studied.

| Sample | Equivalent particle diameters (μm) 10% | 50% | 90% | Screening diamagnetism at 4.2 K (%) | $\lambda(0)$ (μm) |
|---|---|---|---|---|---|
| $A$ | 0.4 | 1.1 | 3.2 | $12.5 \pm 1$ | $0.63 \pm 0.04$ |
| $B$ | 1.6 | 3 | 5 | $27.2 \pm 2$ | $0.61 \pm 0.04$ |
| $C$ | 1.5 | 7.6 | 20 | $46.5 \pm 2$ | $0.73 \pm 0.05$ |
| $D$ | 3 | 9 | 23 | $57 \pm 3$ | $0.68 \pm 0.08$ |
| $E$ | | a | | $77 \pm 5$ | a |

[a](170–230 mesh) particle size distribution not measured.

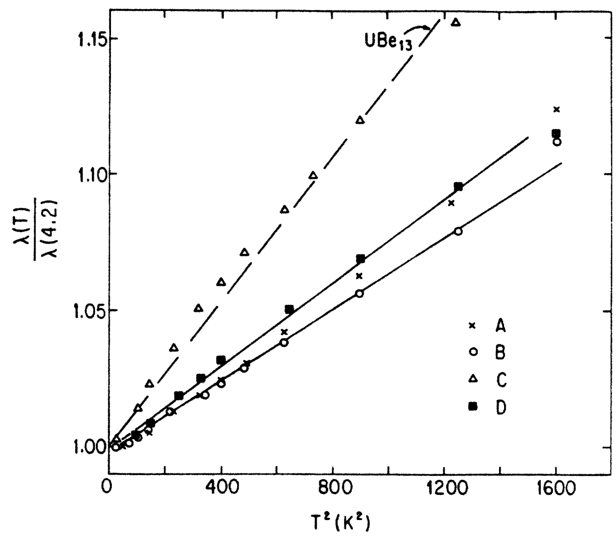


FIG. 3. Low-temperature dependence of $\lambda(T)$ showing the $T^2$ behavior. The dashed line represents data for the heavy-fermion superconductor $UBe_{13}$ scaled to $T_c=91$ K. We have no explanation as to the difference between sample $C$ and the other three samples.

above the free-electron value. Finally, it has recently been shown[16] that in single crystals the anisotropy in the lower critical field ($H_{c1}$) is approximately 10. Within Ginzburg-Landau theory this implies a factor of 3 anisotropy in $\lambda$. Therefore, the value obtained in the present work, which is approximately five times the free-electron value, does not seem to be unusually large.

The difference between the results presented here for $\lambda(T)$ and the muon spin-resonance data in Ref. 3 may be the following. In the latter technique $\lambda$ is determined from the spatial dependence of in the magnetic field around a flux vortex, via line broadening of the resonance line or an enhanced relaxation rate.[3] If there were considerable anisotropy in $\lambda$, as expected in heavy-fermion systems[7] or because of the band-structure anisotropy, then it is probably that the muon technique will be sensitive to the smallest value of $\lambda$, since in the directions where $\lambda$ is small the spatial variation of the magnetic field is largest. On the other hand, in order to completely exclude magnetic flux from the sample, as in our measurements, the particles have to be larger than the *largest* value of $\lambda$.

There are several possibilities of why the temperature dependence of $\lambda$ is different from the BCS behavior. In general, the behavior shown in Figs. 2 and 3 suggests a broad distribution of gap values, with a distribution function extending down to zero energy. While such a distribution can result from a wide distribution of transition temperatures within the specimen, the other explanation is a strongly wave-vector-dependent gap, such as occurs in very anisotropic superconductors, or for higher momentum state pairing.

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