Characterization of superconducting thin films using mm-wave transmission

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ABSTRACT

We present mm-wave transmission as a complementary technique to characterize the properties of superconducting thin films, obtaining information on both the real and imaginary part of the dielectric function. Examples are given to illustrate the strength of the technique to measure the response of dielectric materials and stratified systems. We demonstrate the BCS-behavior of a conventional superconductor NbN, and show furthermore the unconventional behavior in both the absorptive and reactive part of the conductivity of a 20 nm thick $DyBa_2Cu_3O_{7-\delta}$ film.

Keywords: superconducting thin film, mm-wave transmission, conductivity, penetration depth

1. INTRODUCTION

Although high temperature superconductors have proven to be useful for applications, the major breakthrough expected in 1986 has not been established. A large effort has been put into characterizing thin films[1, 2, 3] and understanding the (fundamental) reasons for the existence of phenomena hampering their use, such as their relatively large residual surface resistance. The surface resistance of HTSC thin films and single crystals has been measured using a variety of different techniques. Some of the important ones are cavity perturbation techniques[4, 5, 6] and coherent THz spectroscopy[7, 8] FIR or mm-wave transmission has proven to be valuable in the late fifties when it was used to verify experimentally the existence of the energy gap in several elemental superconductors[9, 10]. In this paper we will show that mm-wave transmission can also be used as a relatively simple way to measure the properties and the quality of a superconducting thin film.

Already from the beginning of high temperature superconductivity[11], it was clear that making high quality films needed for applications was extremely difficult. For instance, attaining and sustaining the right stoichiometry has proven to be a big problem. This became clear in the search for the intrinsic temperature dependence of the penetration depth[2, 4, 12]. For a conventional BCS-superconductor, the intrinsic behavior shows an exponential temperature dependence, caused by the opening of a gap in the excitation spectrum in the superconducting state. This gap is isotropic in momentum space, in the ordinary BCS-description using electron-phonon coupling as the attractive force to form Cooper pairs. However, it was shown by Annet and co-workers in 1991[13], that for a superconductor having zero's (nodes) within the gap, this dependence should be linear. Two years after its prediction the linear behavior was indeed confirmed in single crystals[12], however confirmation in thin films wasn't realized until 1996[14].

Another problem in making thin films is the occurrence of twinning and grain boundaries[15]. Zhang and co-workers showed that for an untwinned $YBa_2Cu_3O_{6.95}$ single crystal the surface resistance is lower[4]. This implies that one reduces the loss in thin films by minimizing the twinning.

However, the problem for thin films with a low (residual) surface resistance is not restricted to the actual deposition and processing. The fundamental, intrinsic properties of the high T_c materials also impose a challenge to the material scientists. It was shown by Nuss et al.[7], using coherent THz spectroscopy, that in entering the superconducting state the optical conductivity is enhanced, reaching a maximum in the temperature range 40-70 K. The maximum in conductivity also appears in the surface resistance since under the conditions generally encountered in HTSC's these are directly proportional. The maximum can be explained by assuming an anomalously large reduction of the quasiparticle scattering rate just below T_c, and is therefore an *intrinsic* source of absorption that one has to deal with. The conductivity and therefore the absorption remains rather high, even at low temperatures. The exact position of the maximum is highly dependent on frequency, and is difficult to be interpreted as a coherence peak, predicted by BCS-theory[16, 17]. Another indication that the coherence factors giving rise to a peak in σ_1 don't play a major role of importance in high T_c's is the absence of the Hebel-Slichter peak in NMR-data. An interesting consequence of reduced scattering is that one is able to *reduce* the peak in R_s and its overall magnitude artificially by *increasing* the impurity content. This effect was demonstrated by Bonn *et al.*, by replacing a fraction of the Cu-atoms by Zn impurities[18].

The discussion about the exact symmetry of the pairing is, in addition to its fundamental importance, also relevant to the application of the cuprates. If, as many people nowadays believe, the symmetry is d-wave[19], this will have important consequences. In this situation, there are points or lines in k-space where the energy gap is zero, implying the presence of quasiparticles already at infinitesimally small energies and temperatures. This means that in a d-wave superconductor even at extremely low temperatures, a residual conductivity will remain. This was proven theoretically by P. Lee[20] who found that a d-wave superconductor will have a universal conductivity at $T = 0$ irrespective of the impurity content at low concentrations. Zhang et al[4] showed that indeed in $YBa_2Cu_3O_{6.95}$ single crystals in both the a- and b-axis direction the residual conductivity is approaching the predicted value.

In view of all of the aforementioned information, it is clear that further studies have to be performed in order to realize a situation where HTSC thin films will surpass the existing conventional superconducting technology.

2. EXPERIMENTAL

In order to obtain amplitude *and* phase information in a direct transmission measurement one needs to use a broadband source. Usually this is a problem in the mm and submm-wave region since conventional sources such as the Gunn oscillators and the impatt diodes have an intrinsic bandwidth of only a few percent. At lower frequencies, where the wavelength of the radiation starts to be very long, one is restricted to use waveguides, furthermore limiting the operational bandwidth. Therefore we have chosen to operate at a frequency where we are able to use quasi-optical methods to manipulate the beam, starting with a source having a relatively broadband output spectrum. The complete experimental setup is shown in fig. 1. As a source

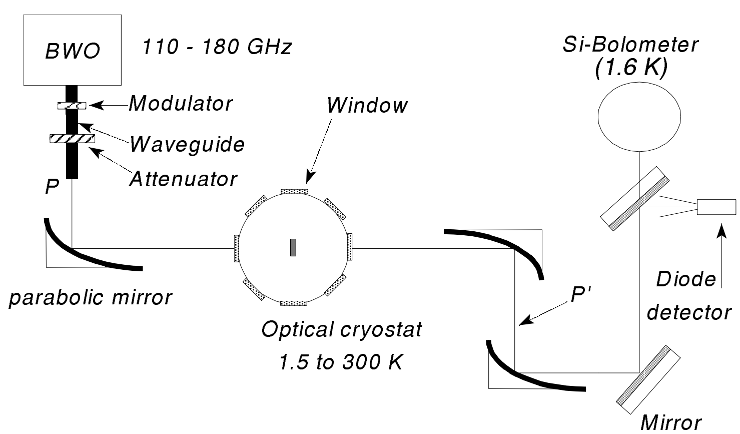

Figure 1: Experimental Setup

we use a Backward Wave Oscillator (BWO). Its useful range of radiation is from 110 to 180 GHz, having a bandwidth of nearly 50 %. The frequency of the radiation is continuously tunable by changing the high voltage (0.5 - 1.5 kV). The range of frequencies enables us to measure complete Fabry-Perot resonant spectra of our samples, thereby yielding complete phase information via the amplitude and position of the peaks. The BWO-output first traverses a modulator, creating the ac-response necessary for the detector, and then an attenuator, used to avoid a nonlinear response of the detector. Next the radiation is coupled out of the waveguide using a Gaussian horn, and treated thereafter quasi-optically. The beam is focused into the cryostat through a quartz window, onto the (superconducting) thin film and subsequently picked up using an off-axis parabolic mirror, placed slightly away from the focal point. This creates a second image P′ (1:1) which is utilized for room temperature measurements. Finally, the transmitted radiation is focused onto either one of two detectors, a highly sensitive but slow Si-bolometer operating at 1.6 K, or a fast, but less sensitive waveguide diode detector. For all measurements presented here, we have used the Si-bolometer, providing a large dynamic range in conjunction with the BWO (output power several tens of milliwatts).

The NbN-film of 55 nm thickness was deposited on an MgO substrate using DC reactive magnetron sputtering[21]. This was done in a gas composition of 3.0% CH_4 / 30.0 % N_2 / Ar, at a temperature of approximately 840 °C. T_c was enhanced to 16.5 K, by the inclusion of carbon. The resistivity ratio (300 K/ 16.5 K) was close to unity.

The 20 nm thick $DyBa_2Cu_3O_{7-\delta}$ film was deposited by RF sputtering on a $LaSrO_3$ substrate using the (100) surface. The substrate temperature was 745 °C while a mixture of argon and oxygen gas was used, at pressures of 105 and 45 mTorr respectively. After the deposition the sample was annealed in 200 mTorr oxygen for 30 minutes at 450 °C. The quality of the surface was checked using X-ray diffraction, showing a very good crystallization.

During measurements three sequential scans as a function of frequency are taken at a fixed temperature, namely sample (film + substrate), bare substrate and a reference aperture. The latter is used to yield *absolute* transmission coefficients for both sample and substrate, which are then used in the rest of the analysis. The transmission through a two layer system is exactly described using the Fresnel equations:

$$t = \frac{\tau_{02} e^{i\psi} t_{20}}{1 - r_{20}\rho_{20} e^{2i\psi}}, \qquad \psi = k d_{subs} p \tag{1}$$

where k is the wave vector of the incident radiation, p the complex index of refraction of the substrate and:

$$\tau_{02} = t_{01} e^{i\phi} \frac{1}{1 - r_{10} e^{i\phi} r_{12} e^{i\phi}} t_{12}, \qquad \phi = k d_{film} \sqrt{\epsilon} \tag{2}$$

$$\rho_{02} = r_{01} + t_{01} e^{2i\phi} r_{12} \frac{1}{1 - r_{10} e^{i\phi} r_{12} e^{i\phi}} t_{10} \tag{3}$$

The dielectric function ϵ is defined in eq. 5 and the reflection and transmission coefficients at each interface are given by:

$$r_{ij} = \frac{n_i - n_j}{n_i + n_j} \quad , \quad t_{ij} = \frac{2n_i}{n_i + n_j} \tag{4}$$

The multiple reflections in the substrate are incorporated in the phase factor $e^{i\psi}$, while a similar contribution from the film is included in a phase factor e^{ϕ} incorporated in the transmission and reflection coefficients τ_{02} and ρ_{20}. The same equation can be used to model the transmission through the bare substrate, simply by setting $d_{film} = 0$. We thus *experimentally* obtain the values for both real and imaginary part of the refractive index of the substrate, which are subsequently used when we analyze the transmission through the two-layer system. For the film we use the well-known two-fluid description first put forward by Gorter and Casimir[22].

$$\epsilon = \epsilon_\infty - \frac{\omega_{ps}^2}{\omega^2} + \frac{4\pi i \sigma_n(\omega)}{\omega} \tag{5}$$

The optical conductivity σ_1 at these low frequencies equals $1/\rho_{dc}$. Also, at low temperatures the superfluid term in eq. (5) dominates ϵ' which is much larger than ϵ'' for a superconductor. This enables us to obtain an absolute value for the penetration depth using ω_{ps} [cm^{-1}] $= 1/2\pi\lambda$ in addition to its temperature dependence.

3. RESULTS

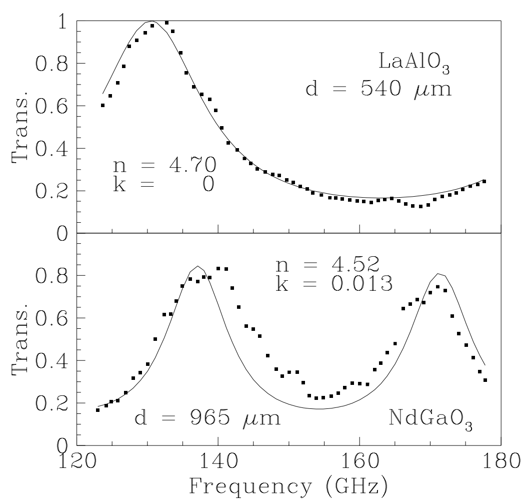

Figure 2: Fabry-Perot resonance spectra for two perovskite substrate materials, $LaAlO_3$ (top) and $NdGaO_3$ (bottom).

In fig. 2 we show the frequency response of two dielectrics, commonly used as substrates for high T_c thin films, $LaAlO_3$ and $NdGaO_3$. We see that the Fabry-Perot resonances are very well described by the transmission calculated using eq. (1). The response of $NdGaO_3$ was measured in the early stages of the setup while the $LaAlO_3$ which was measured recently, showing the improved performance. From the amplitude and the position of the maxima in transmission we can obtain both real and imaginary part of their refractive index. For $LaAlO_3$ the maximum transmission is equal to 1, showing that the absorption in this material can be neglected at these frequencies (4 - 6 cm $^{-1}$), while $n = 4.70$. In case of $NdGaO_3$, the maximum amplitude is slightly reduced, indicative of a small absorption, and the fringes are closer together due to the larger thickness, since the important parameter determining the phase is the product knd. The optical constants are $n = 4.52$ and $k = 0.013$.

In fig. 3 the transmission of a 55 nm thick NbN film on an MgO substrate is shown as a function of frequency for several temperatures, both above and below T_c. The peak in the interference spectrum is determined by the MgO

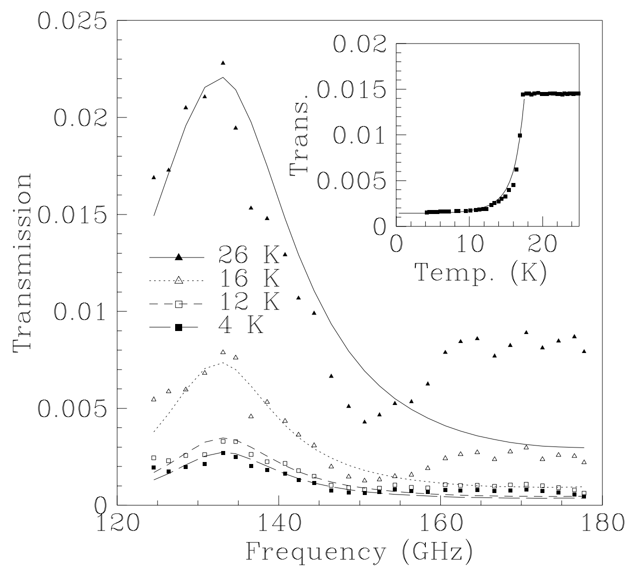

Figure 3: Transmission of NbN on MgO (thickness = 55 nm, T_c = 16.5 K) for 4 different temperatures (4 K: solid squares, 12 K: open squares, 16 K: open triangles and 26 K: solid triangles) together with their fit. Inset: temperature dependence at 140 GHz together with a BCS-fit using $\sigma_1(17K) = 15000\ \Omega^{-1}cm^{-1}$ and $\lambda_L = 400nm$.

substrate having $n = 3.43$ and $k = 0$. We are able to fit the spectra using the two fluid description of equation (5). As expected for a metallic film, $\epsilon'' \gg \epsilon'$, while in the superconducting state the opposite is valid, $\epsilon' \gg \epsilon''$. For the fit we have focused our attention on the main peak around 135 GHz. It is not clear if the poor fit at higher frequencies is caused by an intrinsic property of the NbN film or experimental problems such as a modified standing wave pattern. This is still subject to further research. Notice furthermore that the interference pattern shows no major changes other than a reduced amplitude in the superconducting state.

In the inset of fig. 3 the temperature dependence at one particular frequency (140 GHz) is plotted. In this way the dramatic change in transmission at T_c is more easily observed. The temperature dependence of the transmission coefficient can be fitted nicely using the assumptions that λ(T) can be described by the Gorter-Casimir relation[16], σ_1(T) follows the Mattis-Bardeen relations[23] and 2Δ / kT = 4.0. The only adjustable parameters used in the calculation were the normal state conductivity (σ_1(17 K) = 15000 Ω^{-1}cm^{-1}) determining the transmission at 17 K and the London penetration depth (λ_L = 400 nm) giving the transmission at low temperatures. The penetration depth is somewhat larger than the lowest reported value of 194 nm[24], presumably due to grain boundary formation in the film.

In fig. 4 the frequency dependence of the transmission through a 20 nm thick $DyBa_2Cu_3O_{7-\delta}$ film is shown for several temperatures. One of the most

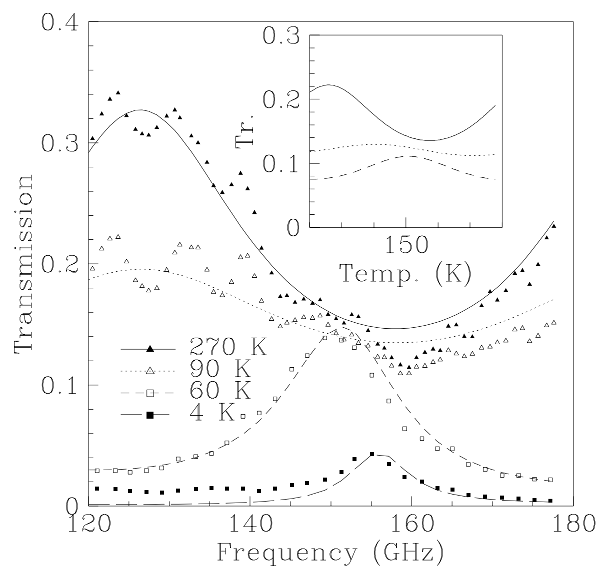

Figure 4: Transmission of $DyBa_2Cu_3O_{7-\delta}$ on $LaAlO_3$ (thickness = 20 nm, T_c = 86 K) for 4 different temperatures (4 K: solid squares, 60 K: open squares, 90 K: open triangles and 270 K: solid triangles) together with their fit. Inset: Transmission of a thin metallic film for three conductivities. (3000 S/cm: solid line, 5000 S/cm: dotted line, 7000 S/cm: dashed line)

striking features is the altered phase at lower temperatures. It is tempting to ascribe this change to the onset of superconductivity, however even for an ordinary metallic film one can observe similar behavior when the conductivity is enhanced. This situation is modeled using the normal state parameters of

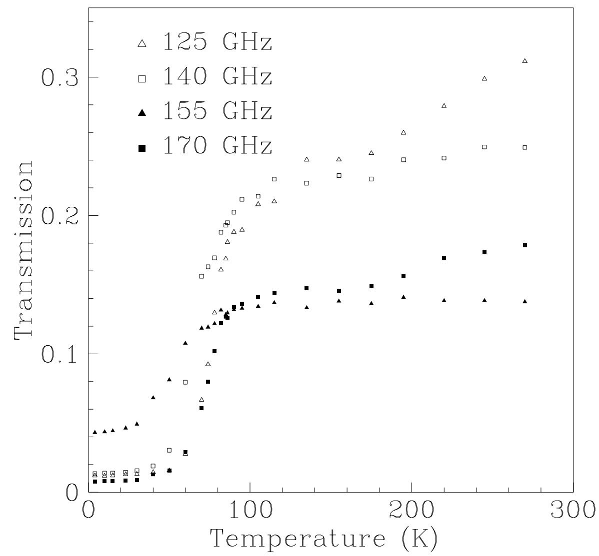

Figure 5: Temperature dependence of the transmission for $DyBa_2Cu_3O_{7-\delta}$ for 4 different frequencies, illustrating the effect of interference on fixed frequency scans.

our $DyBa_2Cu_3O_{7-\delta}$ film, just changing the conductivity from 3000 $\Omega^{-1}cm^{-1}$ to 7000 $\Omega^{-1}cm^{-1}$. The result is depicted in the inset of fig. 4. We can, however, conclude from this that the real part of the conductivity of the $DyBa_2Cu_3O_{7-\delta}$ film is enhanced, even in the superconducting state. This is a result typical for the cuprates, and we will return to this point later in the paper.

From fig. 4 it is evident that taking data over a broad frequency range is essential. In fig. 5 we have plotted the temperature dependence of the transmission coefficient at 4 fixed frequencies. It is clear that the curves are very different, but these differences can be taken into account using the interference effects in the substrate described by eq. (1). The physical properties resulting from this analysis are plotted in figures 6 and 7.

In fig. 6 the real part of the conductivity σ_1 ($\sim \epsilon''$) and the real part of the dielectric function, ϵ', are presented. Both quantities show a steep rise when the temperature drops below T_c. For comparison, the conductivity used for the fitting of the NbN data in fig 3 is shown (solid line, scaled to σ_1 (90 K)). The latter was calculated using the Mattis-Bardeen relations, and vanishes for low temperatures as expected. The rise in conductivity has been observed before both in $YBa_2Cu_3O_{7-\delta}$ single crystals[25] and $YBa_2Cu_3O_{7-\delta}$ thin films[7]. It was explained by an anomalous reduction of quasiparticle scattering (Γ) in entering the superconducting state. Since $\sigma_1 \sim \omega_{pn}^2/\Gamma$, two competing effects determine its temperature dependence. Below T_c the density of normal carriers will be reduced thereby reducing the plasma frequency, while the scattering of quasiparticles may also be re-

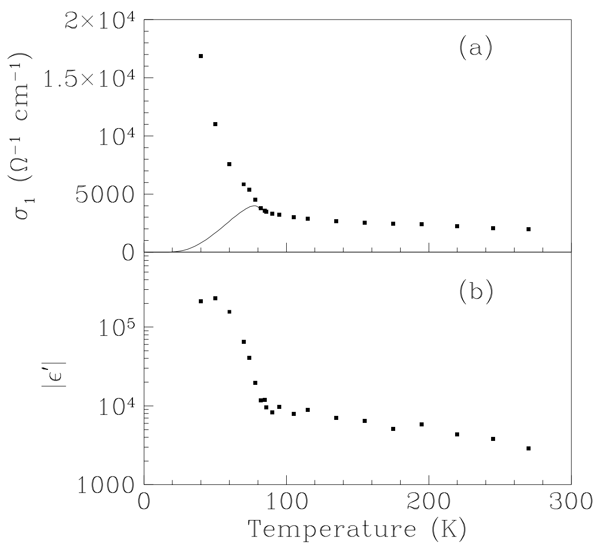

Figure 6: Temperature dependence of the optical conductivity σ_1 (a) and $|\epsilon'|$ (b) for the 20nm thick $DyBa_2Cu_3O_{7-\delta}$ film. The solid line shows the conductivity of the NbN film, scaled to $\sigma_1(90K)$.

duced when the temperature is lowered. Having two different temperature scales produces a maximum in the conductivity. This maximum also resembles a BCS coherence peak but shows a different temperature and frequency behavior than anticipated. An even *more* pronounced "jump" can be seen in $|\epsilon'|$, providing additional support for a reduced scattering rate, since $|\epsilon'| \sim \omega_{pn}^2/\Gamma^2$.

In fig 7a the inverse of the dynamical conductivity is plotted. This should resemble the dc-resistivity for low frequencies. The typical linear temperature dependence is evident. From the fit we can immediately see that the intercept with the x-axis is non-zero, indicative of residual scattering at low temperatures. This additional contribution to the resistivity is not simply temperature *in*dependent since also the slope is larger than the values known from single crystals (1.05 $\mu\Omega$cm/K instead of 0.45 $\mu\Omega$cm/K). In the lower panel (b) the penetration depth is plotted for temperatures $< 50K$. We assume that at low temperatures the contribution of σ_n in eq. 5 to the real part of ϵ can be neglected, resulting in a frequency independent penetration depth. Upto 30 K λ follows a quadratic temperature dependence. The deviation occurring at higher temperatures could be indicative of a transition to another dependence but could also be explained by a stronger influence of ϵ'' complicating the analysis. The London penetration depth is rather large (370 nm), in agreement with findings of de Vaulchier *et al.*[14] demonstrating

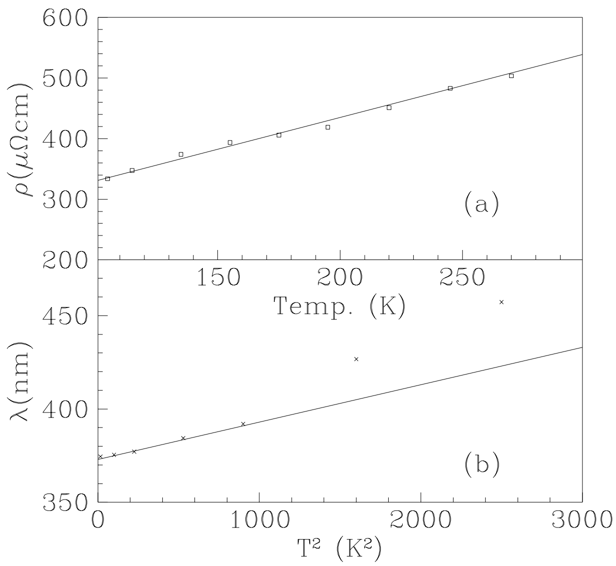

Figure 7: Temperature dependence of the resistivity (a) and the penetration depth (b) for the 20nm thick $DyBa_2Cu_3O_{7-\delta}$ film.

the coexistence of the T^2 dependence and a large λ_L.

4. CONCLUSIONS

We have shown that mm-wave transmission is a useful technique to study and characterize superconducting thin films, yielding absolute information about both real and imaginary part of the dielectric response function. This was illustrated by demonstrating the BCS-behavior expected in NbN. On the other hand, unconventional non-BCS behavior was observed in both the real and imaginary part of the conductivity for a $DyBa_2Cu_3O_{7-\delta}$ thin film. Its conductivity σ_1 shows a maximum in the temperature dependence due to a strongly reduced scattering of quasiparticle scattering below T_c, while the penetration depth follows a T^2 dependence. In conjunction with this we found a large λ_L of 370 nm, supporting the assumption that the quadratic dependence is due to extrinsic sources.

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