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In-plane microwave conductivity of the single-layer cuprate $Tl_2Ba_2CuO_{6+\delta}$

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We have measured the in-plane microwave conductivity of nearly optimally doped single crystals (T_c=78 K) of $Tl_2Ba_2CuO_{6+\delta}$ (Tl-2201) at 14.4, 24.8, and 35.9 GHz using cavity perturbation methods. At low temperatures, the in-plane penetration depth has a strong, linear temperature dependence, indicative of an unconventional pairing state with line nodes. The real part of the conductivity shows a broad, frequency-dependent peak near 30 K, similar to that seen in $YBa_2Cu_3O_{7-\delta}$ and $Bi_2Sr_2CaCu_2O_8$ crystals. With tetragonal crystal symmetry and a single CuO_2 plane per unit cell, Tl-2201 is the simplest structure so far to display these features. [S0163-1829(97)50246-3]

In recent years numerous careful experiments have been made on the cuprate superconductors and, with improvements in sample quality, many of the strange phenomena observed in these materials are now widely accepted as intrinsic. In particular, there is strong evidence for an unconventional pairing state, predominantly of $d_{x^2-y^2}$ symmetry.[1] Constrained by the suitability of currently available materials, this hypothesis has been most thoroughly tested in the hole-doped compounds, for under- to optimal doping. In this context, we present measurements of the in-plane penetration depth λ and surface resistance R_s of $Tl_2Ba_2CuO_{6+\delta}$ (Tl-2201).

Surface impedance ($Z_s = R_s + iX_s$) measurements probe the complex conductivity ($\sigma = \sigma' - i\sigma''$) of a superconductor as a function of temperature and frequency. In the case of local electrodynamics, which applies to the cuprates (at all but the lowest temperatures these are in the *London limit* where the Pippard coherence length $\xi_0 \ll$ carrier mean free path $l \ll \lambda$), the relationship between Z_s and σ is simple: $Z_s = (i\omega\mu_0/\sigma)^{1/2}$. At low frequencies and at temperatures not too close to T_c (so that $\sigma' \ll \sigma''$) we can accurately make the approximations $R_s \approx \frac{1}{2}\mu_0^2\omega^2\sigma'\lambda^3$ and $X_s \approx \omega\mu_0\lambda$. It is usual to interpret the complex conductivity in terms of a two-fluid model and various authors[2,3] have discussed the validity of partitioning the conduction electron density n into normal and superfluid fractions f_n and f_s ($f_n + f_s = 1$) and conclude that this is appropriate in the London limit. In this case, the conductivity is written as $\sigma' - i\sigma'' = (ne^2/m)[f_n/(1/\tau + i\omega) + f_s/i\omega]$, where $1/\tau$ is the effective normal fluid scattering rate.

Microwave measurements have been important in establishing the nature of cuprate electrodynamics, with penetration depth data from high-quality $YBa_2Cu_3O_{7-\delta}$ (YBCO) crystals[4] initially providing some of the clearest evidence of an unconventional order parameter. In YBCO, a linear temperature dependence of the in-plane penetration depth at low temperature was observed and indicated the presence of low-lying excitations, consistent with line nodes in the pairing state. Using untwinned crystals, this behavior was later shown to occur *separately* for currents flowing in the a and b directions,[5] suggesting that the unconventional response was not due solely to the CuO chain layers. Recent measurements on $Bi_2Sr_2CaCu_2O_8$ (BSCCO) single crystals[6,7] also show $\Delta\lambda(T) \propto T$ at low T and support this view; as in YBCO, BSCCO has CuO_2 bilayers, but CuO chain layers are absent. It seems likely that structural variations between the different compounds are affecting the superconductivity only in detail and that a coherent description of these materials may emerge as further measurements reveal the intrinsic properties of other compounds.

Surface resistance data also contribute significantly to our current understanding of the cuprates. Measurements made on high-purity YBCO crystals by Bonn *et al.*[8] show that R_s falls sharply by several orders of magnitude on cooling through T_c. At lower temperatures, R_s rises again, with a small bump at 45 K, before decreasing to a residual value which can be as low as 60 $\mu\Omega$ at 35 GHz in untwinned crystals.[5] The values of $\sigma'(T)$ deduced from the data display a broad peak near the same temperature and a two-fluid interpretation shows that τ rises rapidly on entering the superconducting state (suggesting that inelastic scattering in the normal state is primarily of electronic origin), before saturating at intermediate temperatures at a limit that has been attributed to residual impurity scattering. (The reproducibility of this effect suggests a more intrinsic origin, and it is likely that in the best samples the rise in τ appears to be curbed, instead, when the carriers enter the *anomalous skin effect* regime,[2] where $l > \lambda$.) Measurements on high-quality BSCCO crystals[6] also reveal a broad peak in $\sigma'(T)$ but do not exhibit the nonmonotonic $R_s(T)$ that is characteristic of the best YBCO samples. This, as well as a higher residual R_s, means that BSCCO has more in common with YBCO doped with small amounts of impurities, which may be due to slight structural imperfections in the material.

To test and extend these ideas, we have performed surface impedance measurements on single crystals of Tl-2201. Structurally, Tl-2201 is one of the simplest cuprates, with tetragonal crystal symmetry and a single CuO_2 layer per unit cell. Each CuO_2 plane is widely separated from neighboring planes by thick Tl-O bilayers, resulting in highly anisotropic transport properties[9] ($\rho_c/\rho_{ab} > 1000$). Recently, Tl-2201 thin films on tetra-crystal substrates[10] have been used as a phase sensitive probe of the order parameter, with the conclusion that Tl-2201 has pure d-wave pairing symmetry. It appears that the tetragonal structure of Tl-2201 is playing an important role here, as a recent c-axis tunneling experiment on YBCO,[11] an orthorhombic material, clearly indicates a small s-wave component in the YBCO pairing state. This, and the ability to move from under- to overdoping in a single material, suggests Tl-2201 as a model system for the investigation of d-wave superconductivity. In contrast to other cuprates, Tl-2201 is also a very clean material; $l \sim 10^3$ Å is estimated from direct measurements of the resistivity at low temperature.[12] (In most cuprate materials, there is some disorder in the charge reservoir layers. In tetragonal Tl-2201, the disorder is Cu substitution for Tl and oxygen nonstoichiometry. Both of these occur in the Tl-O layers, which are separated from the CuO_2 layers, reducing the effects of impurity potentials on the in-plane charge dynamics.)

Single crystals of Tl-2201 were grown using a self-flux method in alumina crucibles and annealed in flowing 5% H_2/Ar gas at 420 °C for 10 days to obtain near optimum doping. Although as-grown Tl-2201 platelets are ideal candidates for microwave work, with clean, nondeformed edges and shiny, flat surfaces (the annealing process introduces slight roughening), microwave measurements have not previously been made on them. The small size of the crystals, typically less than 0.5×0.5 mm^2, requires a precise measurement to resolve the low-temperature surface impedance. The superconductivity of Tl-2201 is also very sensitive to oxygen content; addition of just 0.1 oxygen atom/unit cell reduces T_c from optimal ($\sim$85 K) to zero.[14] This allows the crystals to be overdoped easily but means that small inhomogeneities in oxygen content lead to an observable broadening of the superconducting transition, a serious concern because it calls into question the validity of measurements made at temperatures well away from T_c. Here we focus on results from the crystal with the sharpest microwave transition, a small ($0.3\times0.15\times0.01$ mm^3) single crystal, near optimum doping, with T_c=78 K. Away from the transition, and particularly at low temperatures, the results for this crystal agree well with those of other, less homogeneous samples, for which the transitions were broader.

The surface impedance measurements were made by cavity perturbation of high Q resonators, using techniques described in detail elsewhere.[6,13] To enable data to be taken at multiple frequencies, three different resonators were used in all; at 24.8 and 35.9 GHz, standard cylindrical superconducting Nb cavities were employed and, to improve filling factor, a sapphire dielectric disk resonator in a superconducting enclosure was used to make the 14.4 GHz measurement. (Due to the extreme sensitivity of resonant frequency to sample movement in the dielectric resonator, only R_s measurements can be made at 14.4 GHz.) In each case, the resonator was maintained at 4.2 K while the sample was heated independently on a movable sapphire hot finger, reducing systematic error.

All measurements were made with the microwave H field oriented along the crystal c direction, to induce screening currents confined primarily to the a-b plane. The validity of this assumption has been discussed in Ref. 6, where measurements on BSCCO samples of different aspect ratios were used to show that currents flowing in the c direction were insignificant for this type of measurement. Thermal expansion of the crystal can be another source of systematic error,

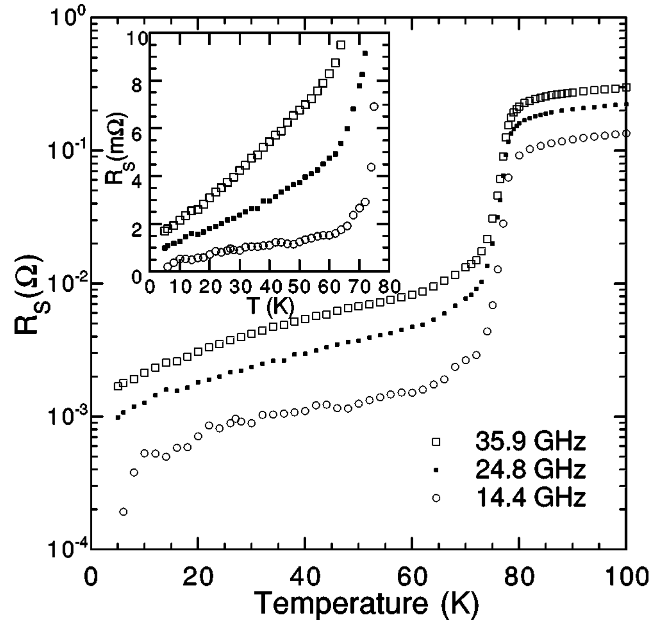

FIG. 1. R_s shows a sharp transition at 78 K and characteristic ω^2 frequency dependence at lower temperatures, indicating good homogeneity. Inset: R_s on a linear scale.

giving an additional contribution to ΔX_s. The ratio of this term to that due purely to changes in λ is proportional to the linear sample dimension. In the absence of thermal expansion data on Tl-2201, we can only comment that the effect has been shown[6] to be insignificant below 30 K in samples of BSCCO as large as 1.2×1.4 mm^2; given the small size of our Tl-2201 crystal, it is unlikely that thermal expansion is contaminating the X_s signal.

The temperature dependence of the resonant frequency f_0 and half-power bandwidth f_B of the TE_{011} mode were measured and related to Z_s using the cavity perturbation formula $\Delta f_B - 2i\Delta f_0 = \Gamma(R_s + i\Delta X_s)$, where $\Delta f_B = f_B(T) - f_B^{\mathrm{empty}}$ and $\Delta f_0 = f_0(T) - f_0(5\text{ K})$, and Γ is an empirically determined calibration factor. It is important to note that while this technique gives R_s absolutely, only changes in X_s are measured; $X_s(0)$ must therefore be obtained by another method. We estimate the uncertainty in R_s to be ± 100 $\mu\Omega$ at 14 and 36 GHz and ± 200 $\mu\Omega$ in the larger 25 GHz cavity, while the error in $\Delta\lambda$ at 36 GHz is about ± 3 Å.

Figure 1 shows the R_s data for all three frequencies. When making measurements on cuprate systems, it is essential to ensure that intrinsic behavior is not being masked by the effects of inhomogeneity. Transition broadening due to nonuniform oxygen content is common in Tl-2201, with the concern that observations made at low temperatures on a sample with a spatial distribution of T_c may not be representative of a system with a single transition temperature. Inhomogeneity often goes undetected by low-frequency methods of characterization; in dc resistivity and low-field magnetization measurements, for instance, a large, abrupt change is seen as soon as a superconducting percolation path appears in the sample. Microwave measurements are much more sensitive to the presence of normal regions in an inhomogeneously oxygenated crystal as, at high frequencies, these regions cannot be completely short circuited by superconducting material. In this crystal, however, the sharp superconducting tran-

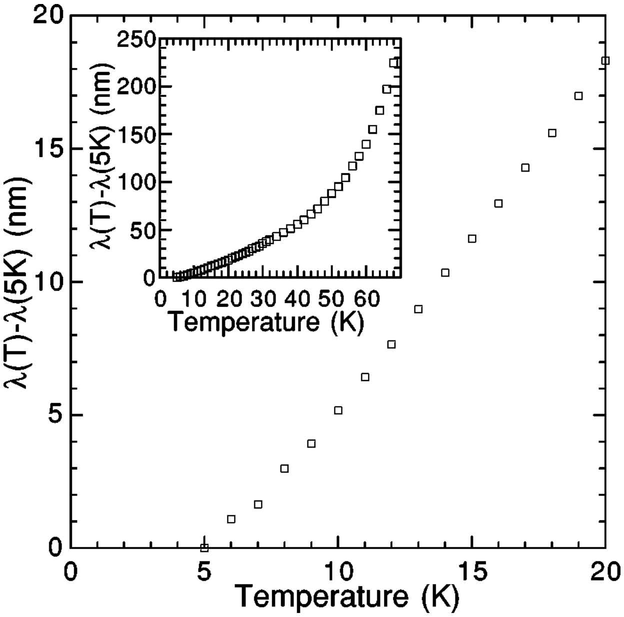

FIG. 2. $\Delta\lambda(T)=\lambda(T)-\lambda(5\text{ K})$ displays a strong linear term at low T. Inset: $\Delta\lambda(T)$ over a wider temperature range.

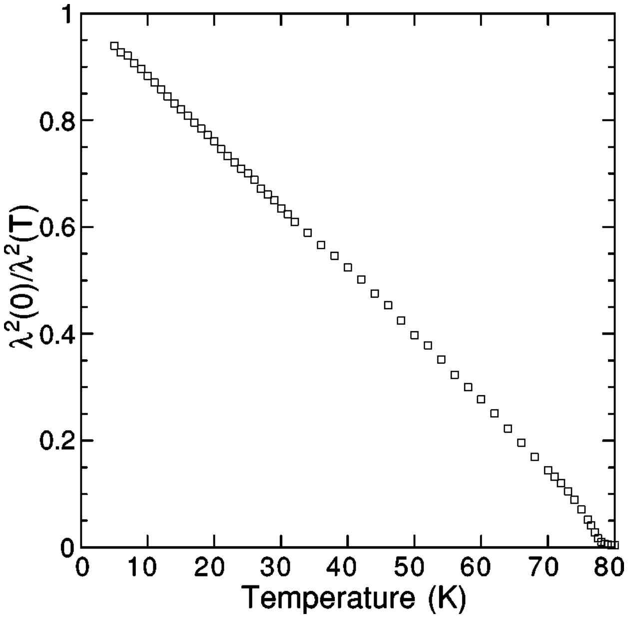

FIG. 3. $f_s(T)=\lambda^2(0)/\lambda^2(T)$ (from σ'') shows a linear temperature dependence over most of the superconducting state, with a rapid downturn near T_c.

sition at 78 K is a clear indication of uniform oxygen content. At temperatures below the transition, R_s scales accurately as ω^2, as expected for a homogeneous superconductor when $\omega\tau$ is small. As temperature is decreased, R_s continues to fall monotonically, reaching a residual value which is comparable to that of the best YBCO and BSCCO crystals.

The $\Delta\lambda(T)=\lambda(T)-\lambda(5\text{ K})$ data for 35.9 GHz are presented in Fig. 2. (The 24.8 GHz data agree well, but are noisier and are not shown.) Below 20 K, $\Delta\lambda(T)\propto T$, with a slope of 13 Å/K. This is larger than the corresponding slopes reported for YBCO (Ref. 4) and BSCCO (Refs. 6 and 7) (4.3 and 10.2 Å/K respectively). Shown in Fig. 3 is $f_s=\lambda^2(0)/\lambda^2(T)$, obtained from σ'' using the local relation between Z_s and σ, which remains valid close to T_c. [$\lambda(0)=1650$ Å is taken from μSR measurements.[15]] f_s has a strong temperature dependence and varies linearly with T over almost the entire range of temperatures of the superconducting state. [Using a larger value of $\lambda(0)$ introduces some curvature into the plot but preserves the linear behavior at low temperatures.] Near T_c there is a sudden downturn in f_s which is well described by an effective medium model of critical fluctuations.[16] The λ data are consistent with calculations for a d-wave pairing state that vanishes along lines of nodes on the Fermi surface but, as λ is insensitive to the phase of the order parameter, the data could be equally well described by a conventional state with sufficient anisotropy. At the lowest temperatures there is some sign of curvature in f_s, although the small size of the crystal means we cannot resolve this precisely. Within the d-wave model, impurity scattering is known to cause a crossover from linear T dependence to quadratic behavior below a temperature T^* proportional to the residual scattering rate.[17] More recently, it has been shown that similar behavior can arise from a crossover to nonlocal electrodynamics at low temperature.[18]

In an orthorhombic superconductor, such as YBCO, we expect mixing of s and d states from the outset, with no second phase transition at lower temperature. In a tetragonal system such as Tl-2201, by contrast, it is possible that the system enters a pure d-wave state at T_c, but that the s state becomes degenerate with the d state at a lower temperature, a mixed state such as an $s+id$ state appearing at a second phase transition. This is, however, not what we observe: we find a single transition in Tl-2201, consistent with the pure d-wave order parameter deduced from recent tetra-crystal junction experiments.[10]

σ' was extracted from the R_s and X_s data using the expression given earlier and the results are shown in Fig. 4. (σ'' should scale as $1/\omega$ in the superconducting state, which we

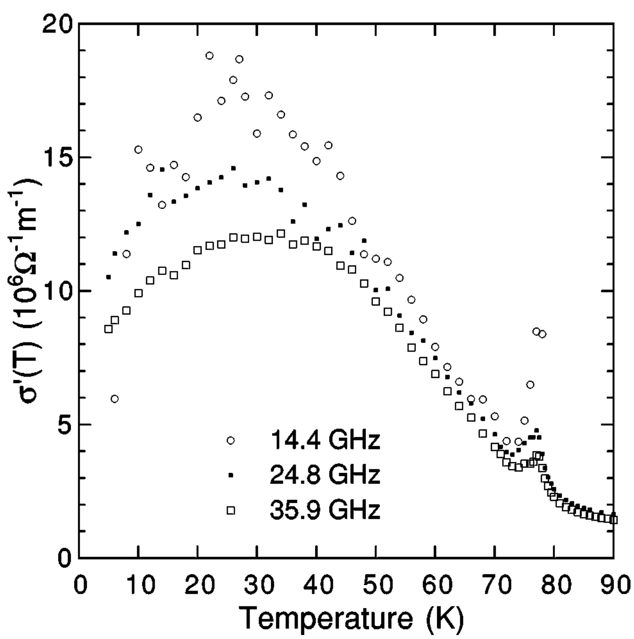

FIG. 4. $\sigma'(T)$ at 14.4, 24.8, and 35.9 GHz displays a broad, frequency-dependent peak at low T.

have assumed in order to obtain σ' at 14 GHz in the absence of X_s data at this frequency.) $\sigma'(T)$ has a sharp peak just below T_c which becomes higher with decreasing frequency. Similar behavior is seen in high-quality YBCO and BSCCO samples and a detailed analysis[16] shows that these peaks can be attributed solely to the inhomogeneity induced by critical fluctuations. Between 50 and 70 K, σ' varies little with frequency; this is as expected for a homogeneous superconductor in the low-frequency limit ($\omega \ll 1/\tau$) and is an important consistency check. At lower temperatures there is a broad peak in $\sigma'(T)$, which finds a natural interpretation within the two-fluid model in terms of an initially rapid rise in τ on cooling through the transition, which is eventually overtaken by falling f_n at low temperature. This picture was first put forward by Bonn and co-workers[8] to explain the temperature dependence of σ' in YBCO, and was borne out by later measurements on samples deliberately doped with impurities.[19] There is at the moment, however, some uncertainty about the experimental situation in YBCO; recent measurements by Srikanth *et al.*[20] show a third peak in $\sigma'(T)$, which is taken as evidence for a multiple component order parameter. The new data differ strongly from the earlier YBCO measurements, which are themselves remarkably similar in form to the σ' data of Tl-2201 and BSCCO.[6] Any model based on two different order parameters arising from coupling between the plane and chain layers, for instance, would not apply to BSCCO and Tl-2201.

In Tl-2201, the frequency dependence of the peak in $\sigma'(T)$, which decreases in height and moves higher in temperature with increasing frequency, suggests that τ rises sufficiently at low T for relaxation of the normal fluid to become visible. Oddly, this is not reflected in σ''; after frequency scaling, the 25 and 36 GHz data agree to within experimental uncertainty ($\sim$2% at 25 GHz). Explanations are being considered and an account of these will be given in the future. At low temperatures σ' approaches a finite intercept. This is seen to varying degrees in all samples and is due, at least in part, to sample imperfection, although there are intrinsic origins of a much smaller residual conductivity within the d-wave model.[21]

In summary, the superconducting electrodynamics of Tl-2201 bear a striking resemblance to those of YBCO and BSCCO; at low temperatures, $\Delta\lambda(T)$ varies linearly with T in the three systems, indicating that, in the cuprates, unconventional pairing is robust in the presence of significant structural variation. The qualitative features of σ' are also similar in the three systems; all display a broad peak in $\sigma'(T)$, suggesting that the rapid collapse in scattering on entering the superconducting state is a feature common to the cuprates.

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[1] J. Annett, N. Goldenfeld, and A.J. Leggett, in *Physical Properties of High Temperature Superconductors V*, edited by D.M. Ginsberg (World Scientific, Singapore, 1996).

[2] J.R. Waldram *et al.*, Phys. Rev. B **55**, 3222 (1997).

[3] A.J. Berlinsky *et al.*, Phys. Rev. B **48**, 4074 (1993).

[4] W.N. Hardy *et al.*, Phys. Rev. Lett. **70**, 3999 (1993).

[5] K. Zhang *et al.*, Phys. Rev. Lett. **73**, 2484 (1994).

[6] S.F. Lee *et al.*, Phys. Rev. Lett. **77**, 735 (1996).

[7] T. Jacobs *et al.*, Phys. Rev. Lett. **75**, 4516 (1995).

[8] D.A. Bonn *et al.*, Phys. Rev. Lett. **68**, 2390 (1992).

[9] N.E. Hussey *et al.*, Phys. Rev. Lett. **76**, 122 (1996).

[10] C.C. Tsuei *et al.*, Nature (London) **387**, 481 (1997).

[11] K.A. Kouznetsov *et al.* (unpublished).

[12] A.P. Mackenzie *et al.*, Phys. Rev. Lett. **71**, 1238 (1993).

[13] R.J. Ormeno *et al.*, Rev. Sci. Instrum. **68**, 2121 (1997).

[14] Y. Kubo *et al.*, Phys. Rev. B **43**, 7875 (1991).

[15] Y.J. Uemura *et al.*, Nature (London) **364**, 605 (1993).

[16] J.R. Waldram *et al.* (unpublished).

[17] Peter J. Hirschfeld and Nigel Goldenfeld, Phys. Rev. B **48**, 4219 (1993).

[18] Ioan Kosztin and Anthony J. Leggett, Phys. Rev. Lett. **79**, 135 (1997).

[19] D.A. Bonn *et al.*, Phys. Rev. B **50**, 4051 (1994).

[20] H. Srikanth *et al.*, Phys. Rev. B **55**, R14 733 (1997).

[21] Patrick A. Lee, Phys. Rev. Lett. **71**, 1887 (1993).